(51) **International Patent Classification⁷:** G01N 27/00

(21) **International Application Number:** PCT/US01/32138

(22) **International Filing Date:** 15 October 2001 (15.10.2001)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
60/240,619    16 October 2000 (16.10.2000)    US
60/246,946    9 November 2000 (09.11.2000)    US

(71) **Applicant** *(for all designated States except US)*: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **MORRIS, Patricia, A.** [US/US]; P.O. Box 532, Montchanin, DE 19710 (US).

(74) **Agent: LANGWORTHY, John, A.**; E.I. Du Pont De Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *without international search report and to be republished upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) **Title:** METHOD AND APPARATUS FOR ANALYZING MIXTURES OF GASES
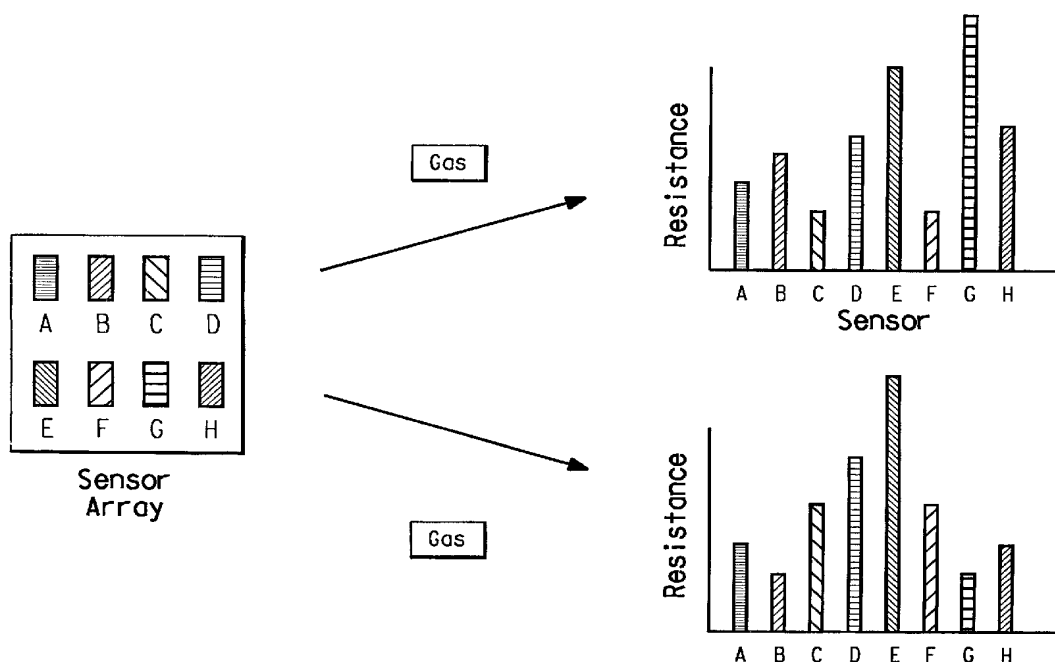
(57) **Abstract:** Disclosed herein is a method and apparatus for analyzing, sensingand measuring the concentrations of various gases, including NOx, hydrocarbons, carbon monoxide and oxygen, in a multi-component gas system using chemical sensorsand chemical sensor arrays. The sensors and sensor arrays use chemo/electro-activematerials to analyze and detect the presence of gases.

TITLE
METHOD AND APPARATUS FOR ANALYZING MIXTURES OF GASES
Field of the Invention
          This application claims the benefit of the filing
5    date of U.S. Provisional Application No. 60/240,619,
     filed October 16, 2000, and of U.S. Provisional
     Application No. 60/246,946, filed November 9, 2000.
          The present invention is a method and apparatus for
     sensing and analyzing certain gases, including $NO_x$,
10   hydrocarbons, carbon monoxide and oxygen in a multi-
     component gas system using chemical sensors and
     chemical sensor arrays.  The sensors and sensor arrays
     use chemo/electro-active materials to detect the
     presence of and/or calculate the concentration of
15   individual gases within the multi-component gas system.
                    Technical Background
          The use of chemical sensing devices to detect
     certain gases is known.  Many attempts have been made
     to find a material with selectivity and sensitivity for
20   a specific gas.  For example, US 4,535,316 discloses a
     resistive sensor for measuring oxygen.  See also H.
     Meixner et al, Sensors and Actuators, B 33 (1996)
     198-202.  It is apparent that different materials must
     .be used for each gas to be detected.  However, when a
25   gas is part of a multi-component system, using one
     material to detect a specific gas is difficult because
     of the cross-sensitivities of the material to the
     various component gases of the mixture.
          One example of a multi-component gaseous system is
30   a combustion gas emission, which can include oxygen,
     carbon monoxide, nitrogen oxides, hydrocarbons, $CO_2$,
     $H_2S$, sulfur dioxide, hydrogen, water vapor, halogens
     and ammonia.  See H. Meixner et al, Fresenius' J. Anal.
     Chem., 348 (1994) 536-541.  In many combustion
35   processes, there is a need to determine whether the gas
     emissions meet requirements established by federal and
     state air quality regulations in various jurisdictions.
     Several types of gas sensors have been developed to
                              1

address this need.  See US 5, 630,920, Friese et al,
which discloses an electrochemical oxygen sensor;
US 4,770,760, Noda et al, which discloses a sensor for
detecting oxygen and oxides of nitrogen; and

5    US 4,535,316, which discloses a resistive sensor for
measuring oxygen.  It would be advantageous to be able
to simultaneously analyze two or more components of a
mixture such as a combustion gas emission, to calculate
concentration for example, in terms only of data

10   generated by direct contact of the gases with a sensor
and without having to separate any of the gases in the
mixture.  Prior art methods do not currently meet this
need.
        Numerous sensors have been disclosed to detect

15   gases evolving from foods and from other relatively low
temperature applications.  See K. Albert et al, *Chem.*
*Rev.*, 200 (2000) 2595-2626.  Arrays of several undoped
and doped tin oxide sensors have also been disclosed
for use in detecting various combustion gases up to

20   450°C.  See C. Di Natale et al, *Sensors and Actuators*,
B 20 (1994) 217-224; J. Getino et al, *Sensors and*
*Actuators*, B33 (1996) 128-133; and C. Di Natale et al,
*Sensors and Actuators*, B 23 (1995) 187-191.  However,
at higher temperatures and in the highly corrosive

25   environment in which one would use chemical sensors to
monitor combustion gases, operating temperature can
alter or impair the performance of the sensor array.
That being the case, high temperature environments
require the use of materials that are both chemically

30   and thermally stable and that maintain measurable
responses to the gases of interest.  The effect of the
operating temperature on the response of tin oxide
bases sensor arrays was studied up to 450°C.  See C.
Di Natale, *Sensors and Actuators* B23 (1995) 187-191.

35   However, materials in addition to those previously
known in the art are still needed to be able to provide
a method and apparatus capable of directly monitoring
the gas emissions of multi-component gas systems at

higher temperatures, such as would be encountered in the operation of combustion gas systems.

Addressing this need would permit the use of a chemical sensor to measure combustion emissions, such as automobile exhausts, and determine whether those emissions meet functional and mandated requirements. In addition, it has surprisingly been found that the method and apparatus of this invention that are useful for analyzing high temperature gases, such as automotive emissions, may be employed with equal effect in analyzing low temperature gases.

Summary of the Invention

This invention provides a method for directly sensing gas components in a multi-component gas system, comprising the steps of: (i) exposing a chemical sensor comprising an array of at least two chemo/electro-active materials to a multi-component gas system, detecting a response, and directly measuring the response of each chemo/electro-active material. Preferably the chemo/electro-active material is a semiconducting material, and the multi-component gas system is a combustion process emission. The response that is measured can be a measurement of capacitance, voltage, current, AC impedance, or DC resistance.

This invention also provides a chemical sensor for directly sensing the presence of gas components in a multi-component gas system, comprising a substrate; an array of at least two chemo/electro-active materials on said substrate; and a means for detecting a response from said chemo/electro-active materials when exposed to said analyte gas component(s) in the system. Preferably the chemo/electro-active material is a semiconducting material, and the multi-component gas system is a combustion process emission. The response that is detected can be an electrical property such as capacitance, voltage, current, AC impedance, or DC resistance. The device can additionally contain a housing, means for measuring the detected responses,

and means for analyzing the results of the measured
responses in order to identify the presence and/or
concentrations of the analyte gas component(s).

This invention also provides for a chemical sensor
device for directly sensing the presence and/or
concentration of gas component(s) in a multi-component
gas system, comprising: a substrate; an array of at
least two chemo/electro-active materials deposited on
said substrate; a means for detecting a change in
electrical properties of said chemo/electro-active
materials upon exposure to said multi-component gas
component(s); means for analyzing the results of the
detected changes in electrical properties in order to
identify the presence and/or concentrations of said gas
component(s); and a housing.  The chemo/electro-active
materials may be semiconducting materials.

In another embodiment, this invention involves an
apparatus for analyzing at least one individual gas
component in a multi-component gas mixture, containing:

(a)  an array of at least two chemo/electro-active
materials connected in parallel circuitry, each
chemo/electro-active material exhibiting a different
electrical response characteristic upon exposure to the
individual gas component than each other chemo/electro-
active material;

(b)  means for determining an electrical response
of each chemo/electro-active material upon exposure of
the array to the gas mixture;

(c)  means for determining a value for the
temperature of the array connected in parallel
circuitry with the chemo/elctro-active materials; and

(d)  means for digitizing the electrical responses
and the temperature value, and calculating a value from
the digitized electrical responses and temperature
value, to perform an analysis of the individual gas
component.

In a further embodiment, this invention involves,
in a multi-component gas mixture having a temperature

of about 400°C or more, an apparatus for calculating the concentration of at least two individual analyte gas components in the mixture, containing:

 (a) an array of at least three chemo/electro-active materials, the array being situated within the gas mixture, and each chemo/electro-active material having a different electrical response characteristic upon exposure to each of the individual analyte gas components than each of the other chemo/electro-active materials;

 (b) means for determining an electrical response of each chemo/electro-active material upon exposure of the array to the unseparated components of the gas mixture; and

 (c) means for calculating the concentration of each of the individual analyte gas components from the electrical responses of the chemo/electro-active materials upon exposure to the multi-component gas mixture only.

In yet another embodiment, this invention involves, in a multi-component gas mixture having a temperature of about 400°C or more, an apparatus for calculating the concentration of at least two individual analyte gas components in the mixture, containing:

 (a) an array of at least three chemo/electro-active materials connected in parallel circuitry, the array being situated within the gas mixture, and each chemo/electro-active material exhibiting a change in electrical resistance upon exposure to each of the individual analyte gas components, wherein at least one chemo/electro-active material, when at a temperature of about 400°C or more, (i) has an electrical resistivity in the range of about 1 ohm-cm to about $10^5$ ohm-cm, and (ii) exhibits a change in electrical resistance of at least about 0.1 percent upon exposure of the material to an analyte gas component, as compared to the resistance before exposure;

5

(b)   means for determining the change in resistance of each chemo/electro-active material upon exposure of the array to the gas mixture;   and

(c)   means for calculating the concentration of each of the individual analyte gas components from the changes in resistance of the chemo/electro-active materials.

In yet another embodiment, this invention involves an apparatus for analyzing at least one individual gas component in a multi-component gas mixture, containing:

(a)   an array of at least two chemo/electro-active materials, each chemo/electro-active material having a different electrical response characteristic upon exposure at a selected temperature to the individual gas component than each of the other chemo/electro-active materials, the electrical response characteristic of each material being quantifiable as a value, wherein the response value of at least one material is constant or varies by no more than about twenty percent during exposure of the material to an individual gas component at the selected temperature for a period of at least about one minute;

(b)   means for determining the electrical response value of each chemo/electro-active material upon exposure of the array to the gas mixture; and

(c)   means for performing an analysis of the individual gas component from the electrical response values.

In yet another embodiment, this invention involves, in a multi-component gas mixture having a temperature of less than about 400°C, an apparatus for analyzing at least one individual gas component in the mixture, containing:

(a)   an array of at least two chemo/electro-active materials, each chemo/electro-active material having a different electrical response characteristic upon exposure at a selected temperature to the individual gas component than each of the other chemo/electro-

active materials, the array being situated within the
gas mixture and having a substantially constant
temperature of about 400°C or more;

5         (b)   means for determining the electrical response
value of each chemo/electro-active material upon
exposure of the array to the gas mixture; and

        (c)   means for performing an analysis of the
individual gas component from the electrical response
values.

10      In yet another embodiment, this invention involves
an apparatus for analyzing at least one individual gas
component in a multi-component gas mixture, containing:

        (a)   an array of first and second chemo/electro-
active materials, each chemo/electro-active material
15 having a different electrical response characteristic
upon exposure at a selected temperature to the
individual gas component than each of the other
chemo/electro-active materials, wherein the
chemo/electro-active materials are selected from the
20 pairings in the group consisting of

           (i) the first material is $M^1O_x$, and the
second material is $M^1_aM^2_bO_x$;

           (ii) the first material is $M^1O_x$, and the
second material is $M^1_aM^2_bM^3_cO_x$;

25            (iii) the first material is $M^1_aM^2_bO_x$, and the
second material is $M^1_aM^2_bM^3_cO_x$;

           (iv) the first material is a first $M^1O_x$, and
the second material is a second $M^1O_x$;

           (v) the first material is a first $M^1_aM^2_bO_x$,
30 and the second material is a second $M^1_aM^2_bO_x$; and

           (vi) the first material is a first
$M^1_aM^2_bM^3_cO_x$, and the second material is a second
$M^1_aM^2_bM^3_cO_x$;

wherein $M^1$ is selected from the group consisting of Ce,
35 Co, Cu, Fe, Ga, Nb, Ni, Pr, Ru, Sn, Ti, Tm, W, Yb, Zn,
and Zr; $M^2$ and $M^3$ are each independently selected from
the group consisting of Al, Ba, Bi, Ca, Cd, Ce, Co, Cr,
Cu, Fe, Ga, Ge, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, Pb,

Pr, Rb, Ru, Sb, Sc, Si, Sn, Sr, Ta, Ti, Tm, V, W, Y, Yb, Zn, and Zr, but $M^2$ and $M^3$ are not the same in $M^1_a M^2_b M^3_c O_x$; a, b and c are each independently about 0.0005 to about 1, provided that a+b+c = 1; and x is a number sufficient so that the oxygen present balances the charges of the other elements in the compound;

(b) means for determining the electrical response of each chemo/electro-active material upon exposure of the array to the gas mixture; and

(c) means for performing an analysis of the individual gas component from the electrical responses.

In yet another embodiment, this invention involves a method for analyzing at least one individual gas component in a multi-component gas mixture, including the steps of:

(a) providing an array of at least two chemo/electro-active materials connected in parallel circuitry, each chemo/electro-active material exhibiting a different electrical response characteristic upon exposure to the individual gas component than each other chemo/electro-active material;

(b) exposing the array to the gas mixture ;

(c) determining an electrical response of each chemo/electro-active material upon exposure of the array to the gas mixture;

(d) determining a value for the temperature of the gas mixture independently of the determination of the electrical responses of the chemo/elctro-active materials; and

(e) digitizing the electrical responses and the temperature value, and calculating a value from the digitized electrical responses and temperature value to perform an analysis of the individual gas component.

In yet another embodiment, this invention involves a method for calculating the concentration of at least two individual analyte gas components in a multi-

8

component gas mixture having a temperature of about
400°C or more, including the steps of:

(a)    providing within the gas mixture an array of
at least three chemo/electro-active materials, each

5      chemo/electro-active material having a different
electrical response characteristic upon exposure to
each of the individual analyte gas components than each
of the other chemo/electro-active materials, wherein at
least one chemo/electro-active material, when at a

10     temperature of about 400°C or more, (i) has an
electrical resistivity in the range of about 1 ohm-cm
to about  $10^5$  ohm-cm, and (ii) exhibits a change in
electrical resistance of at least about 0.1 percent
upon exposure of the material to an analyte gas

15     component, as compared to the resistance before
exposure;

(b)    determining an electrical response of each
chemo/electro-active material upon exposure of the
array to the unseparated components of the gas mixture;

20     and

(c)    calculating the concentration of each of the
individual analyte gas components from the electrical
responses of the chemo/electro-active materials upon
exposure to the multi-component gas mixture only.

25     In yet another embodiment, this invention involves
a method for analyzing at least one individual gas
component in a multi-component gas mixture, including
the steps of:

(a)    providing an array of at least two

30     chemo/electro-active materials, each chemo/electro-
active material having a different electrical response
characteristic upon exposure at a selected temperature
to the individual gas component than each of the other
chemo/electro-active materials, the electrical response

35     characteristic of each material being quantifiable as a
value, wherein the response value of at least one
material is constant or varies by no more than about
twenty percent during exposure of the material to an

individual gas component at the selected temperature
for a period of at least about one minute;

(b)   determining the electrical response value of
each chemo/electro-active material upon exposure of the
array to the gas mixture; and

(c)   performing an analysis of the individual gas
component from the electrical response values.

Description of the Drawings

Figure 1 depicts the sensor array concept.

Figure 2 is a schematic of the pattern of
interdigitated electrodes overlaid with the dielectric
overlayer, forming sixteen blank wells.

Figure 3 depicts the electrode pattern, dielectric
pattern, and sensor material pattern used in preparing
array chips for measurement.

Detailed Description of the Invention

The present invention is a method and apparatus
for directly sensing one or more analyte gases in
multi-component gas systems under variable temperature
conditions.  By "directly sensing" is meant that an
array of gas-sensing materials will be exposed to a
mixture of gases that constitutes a multi-component gas
system, such as in a stream of flowing gases.  The
array may be situated within the gas mixture, and more
particularly within the source of the gas mixture, if
desired.  Alternatively, the array may reside in a
chamber to which the gas mixture is directed from its
source at another location.  The gas mixture may be
inserted in and removed from the chamber by piping,
conduits or any other suitable gas transmission
equipment.

A response may be obtained upon exposure of the
gas-sensing materials to the multi-component gas
mixture, and the response will be a function of the
concentrations of one or more of the analyte gases
themselves in the gas mixture.  The sensor materials
will be exposed substantially simultaneously to each of
the analyte gases, and the analyte gas(es) do not have

10

to be physically separated from the multi-component gas
mixture in order to be analyzed.  This invention can be
used, for example, to detect and/or measure the
concentrations of combustion gases, such as oxygen,
5      carbon monoxide, nitrogen oxides, hydrocarbons such as
butane, $CO_2$, $H_2S$, sulfur dioxide, halogens, hydrogen,
water vaopr and ammonia, at variable temperatures in
automobile emissions.
          This invention is therefore useful at the higher
10     temperatures found in automotive emission systems,
typically in the range of from about 400°C to about
1000°C.  In addition there are a variety of other
combustion processes for which this invention could be
applied, including diesel engines and home heating.
15     These applications require the detection of gases such
as nitrogen oxides, ammonia, carbon monoxide,
hydrocarbons and oxygen at the ppm to per cent levels,
typically in a highly corrosive environment.  This
invention is also useful for detecting gases in other
20     gas systems such as those found in manufacturing
processes, waste streams, and environmental monitoring;
or in systems in which odor detection important and/or
which are at lower temperature, such as in the medical,
agricultural or food and beverage industries.
25          This invention utilizes an array of sensing
materials to analyze the components of a gas system to,
for example, detect the presence of and/or calculate
the concentration of one or more individual analyte gas
components in the system.  By "array" is meant at least
30     two different materials that are spatially separated,
as shown for example in Fig. 1.  The array may contain,
for example, 3, 4, 5, 6, 8, 10 or 12, or other
desirable numbers of, gas-sensing materials.  It is
preferred that there be provided at least one sensor
35     material for each of the individual gases in the
mixture to be analyzed.  Preferably the mole
percentages of the major components of each gas-sensing
material differs from that of each of the others.

11

The sensing materials used are chemo/electro-
active materials. A "chemo/electro-active material" is
a material that has an electrical response to at least
one particular gas. Some metal oxide semiconducting
5    materials, mixtures thereof, or mixtures of metal oxide
semiconductors with other inorganic compounds are
chemo/electro-active, and are particularly useful in
this invention. Each of the various chemo/electro-
active materials used herein preferably exhibits an
10   electrically-detectable response of a different kind
and/or extent upon exposure to an analyte gas of
interest than each of the other chemo/electro-active
materials. As a result, an array of appropriately
chosen chemo/electro-active materials can be used to
15   analyze a multi-component gas mixture, such as by
interacting with an analyte gas, sensing an analyte
gas, or determining the presence and/or concentration
of one or more analyte gases in a gas stream, despite
the presence of interfering gases that are not of
20   interest.

This invention is useful for detecting those gases
that are expected to be present in the gas stream. For
example, in a combustion process, gases that are
expected to be present include oxygen, nitrogen oxides,
25   carbon monoxide, hydrocarbons, ammonia or hydrogen
sulfide. Other gases of interest may include alcohol
vapors, solvent vapors, hydrogen, water vapor, and
those deriving from saturated and unsaturated
hydrocarbons, ethers, ketones, aldehydes, carbonyls,
30   biomolecules and microorganisms.

The measurement of gas concentrations using these
sensor materials can be based on a change in an
electrical property, such as AC impedance, of each of
the materials upon exposure of the materials to a
35   mixture containing one or more analyte gases. Analysis
of a gas mixture can also be performed in terms of
extent of change in other electrical properties of the
sensor materials, such as capacitance, voltage, current

or DC resistance.  Change in DC resistance may be
determined, for example, by measuring change in
temperature at constant voltage.  The change in one of
these illustrative properties of a sensor material is a
5      function of the partial pressure of an analyte gas
within the gas mixture, which in turn determines the
concentration in which the molecules of the analyte gas
become adsorbed on the surface of a sensor material,
thus affecting the electrical response characteristics
10     of that material.  By using an array of chemo/electro-
active materials, a pattern of the respective responses
exhibited by the materials upon exposure to one or more
analyte gas can be used to simultaneously and directly
detect the presence of, and/or measure the
15     concentration of, at least one gas in a multi-component
gas system.  The invention, in turn, can be used to
determine the composition of the gas system.  The
concept is illustrated schematically in Figure 1 and is
exemplified below.
20          To illustrate, consider the theoretical example
below where a response is obtanied, which is depicted
as positive (+), or no response is obtained, which is
depicted as negative (-).  Material 1 responds to Gas 1
and Gas 2, but shows no response to Gas 3.  Material 2
25     responds to Gas 1 and Gas 3, but shows no response to
Gas 2, and Material 3 responds to Gas 2 and Gas 3, but
shows no response to Gas 1.

|        | Material 1 | Material 2 | Material 3 |
|--------|------------|------------|------------|
| Gas 1  | +          | +          | -          |
| Gas 2  | +          | -          | +          |
| Gas 3  | -          | +          | +          |

30          Therefore, if an array consisting of Materials 1,
2 and 3 gives the following response to an unknown gas,

|  | Material 1 | Material 2 | Material 3 |
|---|---|---|---|
| Unknown Gas | + | - | + |

then the unknown gas would be identified as Gas 2.  The
response of each material would be a function of the
partial pressure within the mixture of, and thus the
concentration of, the analyte gas;  and the reponse

5  could be recorded as a numerical value.  In such case,
the numerical values of the responses can be used to
give quantitative information on the concentration
within the mixture of the analyte gas.  In a
multicomponent gas system, chemometrics, neural

10  networks or other pattern recognition techniques could
be used to calculate the concentration of one or more
anylayte gases in the mixture of the system.

The chemo/electro-active material can be of any
type, but especially useful are semiconducting metal

15  oxides such as ZnO, $TiO_2$, $WO_3$, and $SnO_2$.  These
particular materials are advantageous due to their
chemical and thermal stability.  The semiconducting
material can be a mixture of a semiconducting material
with other semiconducting materials, or with any

20  inorganic material, or combinations thereof.  The
semiconducting materials of interest can be deposited
on a suitable solid substrate that is an insulator such
as, but not limited to, alumina or silica and is stable
under the conditions of the multi-component gas

25  mixture.  The array then takes the form of the sensor
materials as deposited on the substrate.  Other
suitable sensor materials include single crystal or
polycrystalline semiconductors of the bulk or thin film
type, amorphous semiconducting materials, and

30  semiconductor materials that are not composed of metal
oxides.

The chemo/electro-active materials used as sensor
materials in this invention may, for example, be metal
oxides of the formula $M^1O_x$, $M^1_aM^2_bO_x$, or $M^1_aM^2_bM^3_cO_x$;

35  or mixtures thereof, wherein

14

$M^1$, $M^2$ and $M^3$ are metals that form stable oxides when fired in the presence of oxygen above 500°C;

$M^1$ is selected from Periodic Groups 2-15 and the lanthanide group;

5    $M^2$ and $M^3$ are independently selected from Periodic Groups 1-15 and the lanthanide group;

a, b, and c are each independently in the range of about 0.0005 to about 1, provided that $a+b+c = 1$; and

x is a number sufficient so that the oxygen
10  present balances the charges of the other elements in the compound.

The metal oxides that contain more than one metal do not have to be a compound or solid solution, but can be a mixture of discrete metal oxides.  They may
15  exhibit composition gradients, and can be crystalline or amorphous.  Suitable metal oxides are those that are

1) when at a temperature of about 400°C or above, have a resistivity of about 1 to about $10^5$ ohm-cm, and preferably about 10 to about $10^4$ ohm-cm,

20  2) show a chemo/electro response to at least one gas of interest, and

3) are stable and have mechanical integrity, that is are able to adhere to the substrate and not degrade at the operating temperature.

25  The metal oxides may also contain minor or trace amounts of hydration and elements present in the precursor materials.

In certain preferred embodiments, the metal oxide materials may include those in which

30  $M^1$ is selected from the group consisting of Ce, Co, Cu, Fe, Ga, Nb, Ni, Pr, Ru, Sn, Ti, Tm, W, Yb, Zn, and Zr;  and/or

$M^2$ and $M^3$ are each independently selected from the group consisting of Al, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu,
35  Fe, Ga, Ge, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Ru, Sb, Sc, Si, Sn, Sr, Ta, Ti, Tm, V, W, Y, Yb, Zn, and Zr, but $M^2$ and $M^3$ are not the same in $M^1{}_aM^2{}_bM^3{}_cO_x$.

In certain other preferred embodiments, the metal oxide materials may include those in which

$M^1O_x$ is $Ce_aO_x$, $CoO_x$, $CuO_x$, $FeO_x$, $GaO_x$, $NbO_x$, $NiO_x$, $PrO_x$, $RuO_x$, $SnO_x$, $Ta_aO_x$, $TiO_x$, $TmO_x$, $WO_x$, $YbO_x$, $ZnO_x$, $ZrO_x$, $SnO_x$ with Ag additive, $ZnO_x$ with Ag additive, $TiO_x$ with Pt additive, $ZnO_x$ with frit additive, $NiO_x$ with frit additive, $SnO_x$ with frit additive, or $WO_x$ with frit additive; and/or

$M^1_aM^2_bO_x$ is $Al_aCr_bO_x$, $Al_aFe_bO_x$, $Al_aMg_bO_x$, $Al_aNi_bO_x$, $Al_aTi_bO_x$, $Al_aV_bO_x$, $Ba_aCu_bO_x$, $Ba_aSn_bO_x$, $Ba_aZn_bO_x$, $Bi_aRu_bO_x$, $Bi_aSn_bO_x$, $Bi_aZn_bO_x$, $Ca_aSn_bO_x$, $Ca_aZn_bO_x$, $Cd_aSn_bO_x$, $Cd_aZn_bO_x$, $Ce_aFe_bO_x$, $Ce_aNb_bO_x$, $Ce_aTi_bO_x$, $Ce_aV_bO_x$, $Co_aCu_bO_x$, $Co_aGe_bO_x$, $Co_aLa_bO_x$, $Co_aMg_bO_x$, $Co_aNb_bO_x$, $Co_aPb_bO_x$, $Co_aSn_bO_x$, $Co_aV_bO_x$, $Co_aW_bO_x$, $Co_aZn_bO_x$, $Cr_aCu_bO_x$, $Cr_aLa_bO_x$, $Cr_aMn_bO_x$, $Cr_aNi_bO_x$, $Cr_aSi_bO_x$, $Cr_aTi_bO_x$, $Cr_aYb_bO_x$, $Cr_aZn_bO_x$, $Cu_aFe_bO_x$, $Cu_aGa_bO_x$, $Cu_aLa_bO_x$, $Cu_aNa_bO_x$, $Cu_aNi_bO_x$, $Cu_aPb_bO_x$, $Cu_aSn_bO_x$, $Cu_aSr_bO_x$, $Cu_aTi_bO_x$, $Cu_aZn_bO_x$, $Cu_aZr_bO_x$, $Fe_aGa_bO_x$, $Fe_aLa_bO_x$, $Fe_aMo_bO_x$, $Fe_aNb_bO_x$, $Fe_aNi_bO_x$, $Fe_aSn_bO_x$, $Fe_aTi_bO_x$, $Fe_aW_bO_x$, $Fe_aZn_bO_x$, $Fe_aZr_bO_x$, $Ga_aLa_bO_x$, $Ga_aSn_bO_x$, $Ge_aNb_bO_x$, $Ge_aTi_bO_x$, $In_aSn_bO_x$, $K_aNb_bO_x$, $Mn_aNb_bO_x$, $Mn_aSn_bO_x$, $Mn_aTi_bO_x$, $Mn_aYb_bO_x$, $Mn_aZn_bO_x$, $Mo_aPb_bO_x$, $Mo_aRb_bO_x$, $Mo_aSn_bO_x$, $Mo_aTi_bO_x$, $Mo_aZn_bO_x$, $Nb_aNi_bO_x$, $Nb_aNi_bO_x$, $Nb_aSr_bO_x$, $Nb_aTi_bO_x$, $Nb_aW_bO_x$, $Nb_aZr_bO_x$, $Ni_aSi_bO_x$, $Ni_aSn_bO_x$, $Ni_aYb_bO_x$, $Ni_aZn_bO_x$, $Ni_aZr_bO_x$, $Pb_aSn_bO_x$, $Pb_aZn_bO_x$, $Rb_aW_bO_x$, $Ru_aSn_bO_x$, $Ru_aW_bO_x$, $Ru_aZn_bO_x$, $Sb_aSn_bO_x$, $Sb_aZn_bO_x$, $Sc_aZr_bO_x$, $Si_aSn_bO_x$, $Si_aTi_bO_x$, $Si_aW_bO_x$, $Si_aZn_bO_x$, $Sn_aTa_bO_x$, $Sn_aTi_bO_x$, $Sn_aW_bO_x$, $Sn_aZn_bO_x$, $Sn_aZr_bO_x$, $Sr_aTi_bO_x$, $Ta_aTi_bO_x$, $Ta_aZn_bO_x$, $Ta_aZr_bO_x$, $Ti_aV_bO_x$, $Ti_aW_bO_x$, $Ti_aZn_bO_x$, $Ti_aZr_bO_x$, $V_aZn_bO_x$, $V_aZr_bO_x$, $W_aZn_bO_x$, $W_aZr_bO_x$, $Y_aZr_bO_x$, $Zn_aZr_bO_x$, $Al_aNi_bO_x$ with frit additive, $Cr_aTi_bO_x$ with frit additive, $Fe_aNi_bO_x$ with frit additive, $Fe_aTi_bO_x$ with frit additive, $Nb_aTi_bO_x$ with frit additive, $Nb_aW_bO_x$ with frit additive, $Ni_aZn_bO_x$ with frit additive, $Ni_aZr_bO_x$ with frit additive, or $Ta_aTi_bO_x$ with frit additive; and/or

$M^1{}_aM^2{}_bM^3{}_cO_x$ is $Al_aMg_bZn_cO_x$, $Al_aSi_bV_cO_x$, $Ba_aCu_bTi_cO_x$, $Ca_aCe_bZr_cO_x$, $Co_aNi_bTi_cO_x$, $Co_aNi_bZr_cO_x$, $Co_aPb_bSn_cO_x$, $Co_aPb_bZn_cO_x$, $Cr_aSr_bTi_cO_x$, $Cu_aFe_bMn_cO_x$, $Cu_aLa_bSr_cO_x$, $Fe_aNb_bTi_cO_x$, $Fe_aPb_bZn_cO_x$, $Fe_aSr_bTi_cO_x$,

5    $Fe_aTa_bTi_cO_x$, $Fe_aW_bZr_cO_x$, $Ga_aTi_bZn_cO_x$, $La_aMn_bNa_cO_x$, $La_aMn_bSr_cO_x$, $Mn_aSr_bTi_cO_x$, $Mo_aPb_bZn_cO_x$, $Nb_aSr_bTi_cO_x$, $Nb_aSr_bW_cO_x$, $Nb_aTi_bZn_cO_x$, $Ni_aSr_bTi_cO_x$, $Sn_aW_bZn_cO_x$, $Sr_aTi_bV_cO_x$, $Sr_aTi_bZn_cO_x$, or $Ti_aW_bZr_cO_x$.

In certain other preferred embodiments, the metal

10    oxide materials may include those which are in an array of first and second chemo/electro-active materials, wherein the chemo/electro-active materials are selected from the pairings in the group consisting of

(i) the first material is $M^1O_x$, and the second

15        material is $M^1{}_aM^2{}_bO_x$;

(ii) the first material is $M^1O_x$, and the second material is $M^1{}_aM^2{}_bM^3{}_cO_x$;

(iii) the first material is $M^1{}_aM^2{}_bO_x$, and the second material is $M^1{}_aM^2{}_bM^3{}_cO_x$;

20        (iv) the first material is a first $M^1O_x$, and the second material is a second $M^1O_x$;

(v) the first material is a first $M^1{}_aM^2{}_bO_x$, and the second material is a second $M^1{}_aM^2{}_bO_x$; and

(vi) the first material is a first $M^1{}_aM^2{}_bM^3{}_cO_x$, and

25        the second material is a second $M^1{}_aM^2{}_bM^3{}_cO_x$;

wherein $M^1$ is selected from the group consisting of Ce, Co, Cu, Fe, Ga, Nb, Ni, Pr, Ru, Sn, Ti, Tm, W, Yb, Zn, and Zr;  $M^2$ and $M^3$ are each independently selected from the group consisting of Al, Ba, Bi, Ca, Cd, Ce, Co, Cr,

30    Cu, Fe, Ga, Ge, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Ru, Sb, Sc, Si, Sn, Sr, Ta, Ti, Tm, V, W, Y, Yb, Zn, and Zr, but $M^2$ and $M^3$ are not the same in $M^1{}_aM^2{}_bM^3{}_cO_x$;  a, b and c are each independently about 0.0005 to about 1, provided that a+b+c = 1; and and x

35    is a number sufficient so that the oxygen present balances the charges of the other elements in the compound.

The sensor materials may optionally contain one or more additives to promote adhesion or to alter the conductance, resistance or selectivity thereof. Examples of additives to promote adhesion are frits,

5    which are finely ground glass, or finely ground inorganic minerals that are transformed into glass or enamel on heating. Illustrative frits include those designated as F2834, F3876, F2967, KH770, KH710 and KH375, available from DuPont iTechnologies. These may

10   be used in amounts of up to 30 volume percent of the composition from which the sensor material is made. Examples of additives to alter the conductance, resistance or selectivity include Ag, Au or Pt as well as frits. If desired, the sensor materials may also

15   contain additives, for example, that catalyze the oxidation of a gas of interest or promote the selectivity for a particular analyte gas, or other dopants that convert an n semiconductor to a p semiconductor, or vice versa. These additives may be

20   used in amounts of up to 30 weight percent of the composition from which the sensor material is made. Any frits or other additives used need not be uniformly or homogeneously distributed throughout the sensor material, but may be localized on or near a particular

25   surface thereof as desired.

Any method of depositing the chemo/electro-active material to the substrate is suitable. One technique used for deposition is applying the semiconducting material on an alumina substrate on which electrodes

30   are screen printed. The semiconducting material can be deposited on top of electrodes by hand painting semiconducting materials onto the substrate, nanopipetting materials into wells, thin film deposition, or thick film printing techniques. Most

35   techniques are followed by a final firing to sinter the semiconducting materials.

Techniques for screen-printing substrates with the electrodes and chemo/electro-active materials are

illustrated in Figures 2-3.  Figure 2 depicts a method
of using interdigitated electrodes overlaid with
dielectric material, forming blank wells into which the
chemo/electro-active materials can be deposited.

5     Figure 3 depicts an electrode screen pattern for an
array of 6 materials which is printed on both sides of
the substrate to provide for a 12-material array chip.
Two of the electrodes are in parallel so it holds only
6 unique materials.  Below that is the screen pattern

10    for the dielectric material, which is screen printed on
top of the electrodes on both side of the substrate to
prevent the material from being fouled by contact with
the gas mixture, such as becoming covered with soot
from an auto, truck, machine or equipment engine, and

15    shorting out.  Below that is the screen pattern for the
actual sensor materials.  This is printed in the holes
in the dielectric on top of the electrodes.  When more
than one material is used in the array the individual
materials are printed one at a time.

20         The sensor materials are interconnected by
conductors, and those conductors are in turn connected
to electrical input and output circuitry.  The
circuitry includes meters, data acquisition means and
other devices as appropriate to measure and record the

25    response exhibited by a sensor material upon exposure
to an analyte gas, to generate a signal in relation to
that response, and to process the signals in a manner
that completes the quantitative analysis of the gas
mixture by presenting a report or display of a result

30    indicating the presence and/or concentration of the
analyte gas.  For example, the several sensors in an
array may be accessed serially by a multiplexer, and
the data retrieved may then be processed on the basis
of the proportionality of the value of an electrical

35    property measured to the concentration of an individual
analyte gas in a multi-component mixture.  The data
acquisition, processing, storage and display system may
include means for conversion from analog to digital

19

format to enable the digitization of the responses of
the sensors and other values, such as the measurement
of temperature.

A response model is constructed using equations in
5      which constants, coefficients or other factors are
derived from pre-determined values characteristic of a
precisely measured electrical response of an individual
sensor material to a particular individual gas expected
to be present as a component in the mixture to be
10     analyzed.  The equation may be constructed in an manner
that takes temperature into account as a value separate
and apart from the electrical responses exhibited by
the sensor materials upon exposure to the gas mixture.
Each individual sensor material in the array differs
15     from each of the other sensors in its response to at
least one of the component gases in the mixture, and
the responses of each of the sensors to each analyte
gas by itself is known.

The gas of interest to which the chemo/electro-
20     active material will be exposed can be a single gas, a
mixture, or one or more gases mixed with an inert gas
such as nitrogen.  Particular gases of interest are
donor and acceptor gases.  These are gases that either
donate electrons to the semiconducting material, such
25     as carbon monoxide, $H_2S$ and hydrocarbons, or accept
electrons from the semiconducting material, such as $O_2$,
nitrogen oxides (commonly depicted as $NO_x$), and
halogens.  When exposed to a donor gas, an n-type
semiconducting material will have a decrease in
30     electrical resistance, increasing the current, and it,
therefore, will show an increase in temperature due to
$I^2R$ heating.  When exposed to an acceptor gas, an
n-type semiconducting material will have an increase in
electrical resistance, decreasing the current, and
35     therefore will show a decrease in temperature due to
$I^2R$ heating.  The opposite occurs with p-type
semiconducting materials.

The geometry of the sensor materials, selection of material, thickness of material, and voltages used can vary and depend on the sensitivity required. The sensor materials are preferably connected in parallel

5     in a circuit to which a voltage of about 1 to about 20, preferably about 1 to about 12, volts is applied across the sensor materials. When performing an analysis of a muti-component gas mixture, it is preferred that each chemo/electro-active sensor material in the array

10    exhibit a different electrical response characteristic than each of the other chemo/electro-active materials in the array upon exposure to an analyte gas component of interest in the mixture.

As noted, the types of electrical response

15    characteristics that may be measured include AC impedance or resistance, capacitance, voltage, current or DC resistance. It is preferred to use resistance as the electric response characteristic of the sensor materials that is measured to perform analysis of a

20    component within the gas mixture. For example a suitable sensor material may be that which, when at at a temperature of about 400°C or above, has a resistivity of at least about 1 ohm-cm, and preferably at least about 10 ohm-cm, and yet no more than about

25    $10^5$ ohm-cm, and preferably no more than about $10^4$ ohm-cm. Such a sensor material may also be characterized as that which exhibits, preferably at a temperature of about 400°C or above, upon exposure to an analyte in the gas mixture, a change in resistance of at least

30    about 0.1 percent, and preferably at least about 1 percent, as compared to the resistance before exposure.

Regardless of the type of response characteristic that is measured for the purpose of analyzing the

35    gaseous component(s) of interest, it is desirable that a sensor material be utilized for which that response value is stable over an extended period of time. When the sensor material is exposed to the analyte, the

21

concentration of the analyte being a function of the
composition of the particular gas mixture in which it
is contained, the response characteristic of the sensor
material will preferably remain constant or vary to
5    only a small extent over an extended period of time at
a constant temperature.  For example, the response
characteristic, if it varies, will vary by no more than
about twenty percent, preferably no more than about ten
percent, more preferably no more than about
10   five percent, and most preferably no more than about
one percent over a period of at least about 1 minute,
or preferably a period of hours such as at least about
1 hour, preferably at least about 10 hours, more
preferably at least about 100 hours, and most
15   preferably at least about 1000 hours.  One of the
advantages of the sensor materials described above is
that they are characterized by this kind of stability
of response.
      In applications in which the gas mixture is above
20   about 400°C, the temperature of the sensor materials
and the array may be determined substantially only, and
preferably is determined solely, by the temperature of
the gas mixture in which the analyste gas(es) are
contained.  This is typically a variable temperature.
25   When higher-temperature gases are being anaylzyed, it
may be desirable to provide a heater with the array to
bring the sensor materials quickly to a minimum
temperature.  Once the analysis has begun, however, the
heater (if used) is typically switched off, and no
30   method is provided to maintain the sensor materials at
a preselected temperature.  The temperature of the
sensor materials thus rises or falls as does the
temperature of the surrounding environment.  The
temperature of the surrounding environment, and thus
35   the sensors and the array, is determined by (or results
from) substantially only the temperature of the gas
mixture to which the array is exposed.

In applications in which the gas mixture is below about 400°C, it may be preferred to maintain the sensor materials and the array at a preselected temperature of about 400°C or above. This preselected temperature may be substantially constant, or preferably is constant. The preselected temperature may also be about 500°C or above, about 600°C or above, or about 700°C or above. This may be conveniently done with a heater incorporated with the array, in a manner as known in the art. The temperature of the gas mixture may also be below about 300°C, below about 200°C, or below about 100°C.

A change of temperature in the array may be indicated by a change in the quantified value of the electrical response characteristic, resistance for example, of a sensor material. At a constant partial pressure in the mixture of a gas of interest, the electrical response characteristic of a sensor material may vary with a change in temperature of the array, and thus the material. This change in the value of the electrical response characteristic may be measured for the purpose of determining or measuring the extent of change of, and thus a value for, temperature. It is preferred that this measurement of temperature be made independently of the determination of the electrical responses of the chemo/electro-active materials. This can be done by connecting the temperature measuring device in parallel circuitry with the sensor materials, rather than in series. A thermocouple or a pyrometer is useful for the purpose of determining the temperature of the array. Particularly if the termperature determining device is a thermistor, typically a material that is not responsive to an analyte gas, the thermistor is preferably made from a different material than the material from which any of the gas sensors is made. Regardless of the method by which temperature or change in temperature is determined, a temperature value or a quantified change

in temperature is a desirable input, preferably in
digitized form, from which an analysis of an analyte
gas in a mixture of gases may be performed.

　　　Unlike various prior-art technologies, in the
5    method and apparatus of this invention, there is no
need to separate the component gases of the mixture for
purposes of performing an analysis, such as by a
membrane or electrolytic cell.  There is also no need
when performing an analysis by means of this invention
10   to employ a reference gas, to bring the response or
analytical results back to a base line value.  With the
exception of preliminary testing to determine a
standardized response value to be assigned to the
exposure of each individual sensor material to each
15   individual analyte gas.  The sensor materials are
exposed only to the mixture that contains an analyte
gas component.  The sensor materials are not exposed to
any other gas to obtain response values for comparison
to those obtained from the analyte.  The analysis of
20   the component gas(es) of interest is therefore
performed only from the electrical responses obtained
upon exposure of the chemo/electro-active materials to
the mixture containing the analyte.  No information
about an anyalte gas is inferred by exposure of the
25   sensor materials to any gas other than the analyte
itself as contained within the mixture.

　　　This invention therefore provides a method and
apparatus for directly sensing the presence and/or
concentration of one or more gases in an multi-
30   component gas system, comprising an array of at least
two chemo/electro-active materials chosen to detect the
gases in a multi-component gas stream.  The array, gas
of interest, gas stream, and chemo/electro-active
materials are as described above.  The multi-component
35   gas system can be at essentially any temperature that
is not so low or so high that the sensor materials are
degraded or the sensor apparatus otherwise
malfunctions.  In one embodiment, the gas system may be

at a lower temperature such as room temperature (about
25°C) or elsewhere in the range of about 0°C to less
than about 100°C, whereas in another embodiment the gas
mixture may at a higher temperature such as in the
5    range of about 400°C to about 1000°C.
         The invention is applicable to gas mixtures that
may be at higher temperatures – gases for example in
combustion streams such as automobile exhausts, diesel
engines and home heating systems.  The invention is
10   also applicable, however, to gas mixtures derived from
other sources, such as in manufacturing processes,
waste streams, and environmental monitoring; or in
systems in which odor detection is important and/or
which are at lower temperature, such as in the medical,
15   agricultural or food and beverage industries.  The gas
mixture may therefore have a temperature that is about
100°C or more, about 200°C or more, about 300°C or
more, about 400°C or more, about 500°C or more, about
600°C or more, about 700°C or more, or about 800°C or
20   more, and yet is less than about 1000°C, is less than
about 900°C, is less than about 800°C, is less than
about 700°C, is less than about 600°C, is less than
about 500°C, is less than about 400°C, is less than
about 300°C, is less than about 200°C, or is less than
25   about 100°C.
         This invention will further comprise means to
determine, measure and record responses exhibited by
each of the chemo/electro-active materials present upon
exposure to the gas mixture.  For example, any means
30   that will determine, measure and record changes in
electrical properties can be used. This may, for
example, be a device that is capable of measuring the
change in AC impedance of the materials in response to
the concentration of adsorbed gas molecules at their
35   surfaces.  Other means for determining electrical
properties can be suitable devices used to measure, for
example, capacitance, voltage, current or DC
resistance.  Alternatively a change in temperature of

the sensing material may be measured and recorded.  The
chemical sensing method and apparatus may further
comprise a means to measure or analyze the detected
gases such that the presence of the gases are
5    identified and their concentrations are measured.
These means can include devices, such as
instrumentation or equipment that is capable of
performing chemometrics, neural networks or other
pattern recognition techniques.  The chemical sensor
10   device will further comprise a housing for the array of
chemo/electro-active materials, the means for
detecting, and a means for analyzing.

The invention also provides a chemical sensor for
directly sensing the presence and/or concentration of
15   one or more gases in an multi-component gas system,
said sensor comprising: a substrate, an array of at
least two chemo/electro-active materials chosen to
detect the predetermined gases in a multi-component gas
stream, and a means to detect changes in electrical
20   properties in each of the chemo/electro-active
materials present upon exposure to the gas system.  The
array, gas of interest, gas stream, chemo/electro-
active materials, and means for detecting are as
described above.

25   The array of sensor materials should be able to
detect an individual gas of interest despite competing
reactions caused by the presence of the several other
components of the multi-component mixture.  For this
purpose, this invention uses a an array of multiple
30   sensor materials, as described herein, each of which
has a different sensitivity for at least one of the gas
components of the mixture to be detected.  A sensors
that has the needed sensitivity, that has the other
attributes described herein, and that can operate in
35   the types of conditions described herein, is obtained
by selection of appropriate compositions of materials
from which the sensor is made.  Various suitable
compositions of materials for this purpose are

described herein.  The number of sensors in the array
is typically greater than or equal to the number of
individual gas components to be analyzed in the
mixture.

5        The following non-limiting examples are meant to
illustrate the invention but are not intended to limit
it in any way.  In the examples provided below, "chip"
is used to describe an alumina substrate comprising an
electrode and sensing material, and dielectric, if a

10  dielectric is used.  The notation "X% A:MO" means that
another inorganic compound (A) has been added at the
specified concentration (X% on an atomic basis) to the
metal oxide (MO).  The term "frit" is used to describe
a mixture of inorganic compounds that usually form a

15  glass at some temperature.
Examples
         Described below are exemplary techniques that may
be used to prepare sensor materials, and to measure
signals using infrared (IR) thermographic and AC

20  impedance techniques.
IR Thermographic Samples and Measurements
         The change in impedance of a sensor material when
exposed to a gas or gas mixture may be determined by
measuring the change in temperature of the material

25  sample by a technique such as infrared thermographic
imaging.
A.   Array Chip Fabrication
         A blank array chip was made by screen printing an
interdigitated electrode pattern, shown in Figure 2,

30  onto an alumina substrate (obtained from Coors Tek, 96%
alumina, 1" x 0.75" x 0.025").  A semi-automatic screen
printer (ETP Electro-dial, Series L-400) was used.  The
electrode paste is available from DuPont iTechnologies,
product #5715.  The electrode screen that was used

35  (obtained from Microcircuit Engineering Corporation)
had an emulsion thickness of 0.5 mil.  After screen
printing, the parts were dried in a convection oven at
120°C for 10 minutes and then fired.  Firing was done

in air using a 10 zone belt Lindberg furnace with a
cycle time of 30 minutes and a peak temperature of
850°C for 10 minutes.  After the electrodes were fired
onto the substrate a dielectric (DuPont iTechnologies,
5    product #5704) pattern, shown in Figure 2, was screen
printed over the electrodes with a screen (Microcircuit
Engineering Corporation), having an emulsion thickness
of 0.9 mil.  The parts were then dried at 120°C for
10 minutes and fired using the same firing cycle as
10   described above.

B.    Semiconducting Metal Oxide Preparation and
Application on the Array Chip

      Approximately 175 mg of the semiconducting metal
oxide powder or the mixture of a semiconducting metal
15   oxide with a suitable glass frit (DuPont iTechnologies
product #F2889 or F3876) or the mixture of the
semiconducting metal oxide powder with other inorganic
compounds was weighed out on to a glass slide with
approximately 75 mg of a suitable medium (DuPont
20   iTechnologies product #M2619) and 1 mg of a suitable
surfactant (DuPont iTechnologies product #R0546).  The
medium and surfactant were mixed together and the metal
oxide powder or mixture was added to the medium and
surfactant gradually to ensure wetting.  If needed, a
25   suitable solvent (DuPont iTechnologies product #R4553)
was added at this time to reduce the viscosity.  The
paste was then transferred to an agate mortar and
pestle for more thorough mixing.  Using a finely
pointed wooden applicator, a very small amount of paste
30   was then placed into one of the wells of the array
chip.  This procedure was repeated with each of the
metal oxide powders or mixtures until all of the wells
on the array chip were filled.  Once the wells on the
array chip were filled with pastes, the array chip was
35   allowed to sit in a closed chamber with a low flow of
$N_2$ gas passing over the chip.  The array chip was then
dried at 120°C for 10 minutes.  Firing was done in air
using a Fisher programmable box furnace with a

1°C/minute ramp rate up to 650°C, where it was held at
temperature for 30 minutes.  The cooling rate was
5°C/minute to room temperature.

C.  Wiring of the Array Chip

5       Lead wires were fabricated using approximately
1.5" of 0.005" platinum wire.  One end of the wire was
bare and the other end was connected to a female RS232
connector.  The bare end of a platinum lead wire was
attached to one of the open conductor pads on the array
10  chip using a conducting paste (Pelco product #16023).
A second lead wire was attached the same way to the
other open conductor pad on the array chip.  The chip
was then allowed to dry for at least 4 hours at 120°C.

D.  IR Thermographic Measurements

15      The test chamber comprised a 2.75" cube containing
input and output valves for gas flow, a 1" MgF window,
two thermocouple feedthroughs and two electrical
feedthroughs.  The electrical feedthroughs provided
connections to the sample heater (Advanced Ceramics,
20  Boralectric heater # HT-42) and the voltage/current
measuring unit (Keithley Instruments model #236).  The
gas flows were regulated using a multi-gas controller
(MKS model #647B).  The sample heater was controlled
using a unit from Hampton Controls (70VAC/700W phase
25  angle).  The infrared camera (Inframetrics PM390) was
focused on the front surface of the array chip using a
100 $\mu$m close-up lens during the measurements.

        Before the measurements were made the sample was
placed inside the test chamber on top of the sample
30  heater.  The female pins on the lead wires connected to
the array chip were then connected to the electrical
feedthrough connected to the voltage/current measuring
unit.  The chamber was closed and placed in the visual
path of the IR camera.  Gas (100 sccm $N_2$, 25 sccm $O_2$)
35  was then allowed to flow into the chamber during
heating of the sample.  Next, the sample was heated
(approximately 10°C/minute) to the desired temperature
and equilibrated before the voltage/current measuring

unit was turned on and a voltage applied. The voltage
was typically adjusted to allow a current flow of
between 10-20 mA through the array.

5 IR thermographic images of the array of materials
were taken 20 minutes after each change in the flows of
the following gases: $N_2$, $O_2$, and gas mixtures as
follows: 1%CO/99% $N_2$, 1% $NO_2$/99% $N_2$ and 1% $C_4H_{10}$/99%$N_2$.
Unless otherwise noted, the content of all gas mixtures
described below is stated in percent by volume. The
10 temperatures of the materials in 2% $O_2$/98% $N_2$ were
subtracted from their temperatures in the other gas
mixtures to determine the temperature signals in the
examples. ThermMonitor 95 Pro, version 1.61
(Thermoteknix Systems, Ltd.) was used to do the
15 temperature subtractions. When exposed to a donor gas,
n-type semiconducting materials will have a decrease in
resistivity, increasing the current and therefore, will
show an increase in temperature due to $I^2R$ heating.
When exposed to an acceptor gas, n-type semiconducting
20 materials will have an increase in resistivity,
decreasing the current and therefore will show a
decrease in temperature due to $I^2R$ heating. The
opposite occurs with p-type semiconducting materials.
<u>AC Impedance Samples and Measurements</u>
25 <u>A.   Semiconducting Metal Oxide Paste Preparation</u>
Approximately 2-3 grams of the semiconducting
metal oxide powder or the mixture of a semiconducting
metal oxide with a suitable glass frit (DuPont
*i*Technologies product #F2889 or F3876) or the mixture
30 of the semiconducting metal oxide with other inorganic
compounds was weighed out with an amount of a suitable
medium (DuPont *i*Technologies product #M2619) sufficient
to provide approximately 40-70 weight % solids. These
materials were then transferred to a muller (Hoover
35 automatic muller, model #M5) where they were mixed
together using a spatula until no dry powder was left.
If needed, a suitable surfactant, such as DuPont
*i*Technologies product #R0546, was added to reduce the

viscosity.  Further mixing was done using the muller
with 500 grams of weight for approximately 6 passes at
25 revolutions per pass.  The finished pastes were then
transferred to containers until needed.

5   B.   Single Sensor Fabrication

        Some of the sensing chips were prepared using a
single material and not arrays of sensing materials.
The single sensing sample chips were made by screen
printing an interdigitated electrode pattern with

10  electrodes, which are 0.4" long and have a 0.008"
spacing onto an alumina substrate (Coors Tek, 96%
alumina, 1" x 1" x 0.025").  A semi-automatic screen
printer (ETP Electro-dial, Series L-400) was used.  The
electrode paste (product #5715) is available from

15  DuPont iTechnologies.  The electrode screen
(Microcircuit Engineering Corporation) had an emulsion
thickness of 0.5 mil.  After printing, the parts were
dried in a convection oven at 120°C for 10 minutes and
then fired.  Firing was done using a 10 zone belt

20  furnace (Lindberg) with a cycle time of 30 minutes and
a peak temperature of 850°C for 10 minutes.  The sensor
material was then screen printed on the substrate using
a screen (Microcircuit Engineering Corporation) with an
open area 0.5" x 0.5".  This screen had an emulsion

25  thickness of 1.0 mil.  After the sensor material was
printed the part was dried in a convection oven at
120°C for 10 minutes.  At this point the part was fired
in air to 850°C for 10-45 minutes using a Lindberg tube
furnace.

30  C.   Sensor Array Fabrication

        A variety of electrode and sensor configurations
can be used to acquire the AC impedance data of the
sensor array.  Described immediately below is the
fabrication of a 12-material array.

35      The sensor array chip was made by screen printing
an electrode pattern (Figure 3) onto an alumina
substrate (Coors Tek, 96% alumina, 2.5" x 0.75" x
0.040").  A semi-automatic screen printer (ETP Electro-

dial, Series L-400) was used. The electrode paste
(product #4597) is available from DuPont *i*Technologies.
The electrode screen (Microcircuit Engineering
Corporation) had an emulsion thickness of 0.4 mil.

5       Note in Figure 3 that two of the sensor pads are in
parallel, so that only six unique sensor material
measurements can be made from this electrode
configuration. After printing, the parts were dried in
a convection oven at 130°C for 10 minutes and then

10      fired. Firing was done in air using a 10 zone belt
furnace (Lindberg) with a cycle time of 30 minutes and
a peak temperature of 850°C for 10 minutes. After the
electrodes were fired onto the substrate a dielectric
(DuPont *i*Technologies, product #QM44) pattern, shown in

15      Figure 3, was screen printed over the electrodes with a
screen (Microcircuit Engineering Corporation), having
an emulsion thickness of 1.0 mil. The parts were then
dried at 130°C for 10 minutes and fired using the same
firing cycle as described above. At this point, each

20      sensor material was screen printed on the substrate
into the wells of the dielectric using the screen
(Microcircuit Engineering Corporation), shown in
Figure 3. This screen had an emulsion thickness of
1.0 mil. After each sensor material was printed the

25      part was dried in a convection oven at 130°C for
10 minutes. After all of the sensor materials (6) were
applied to this side of the sensor, the part was fired
using the same firing cycle as described above. After
this firing step, the above printing, drying and firing

30      steps were repeated on the back side of the substrate
to add 6 more sensor materials to the array chip.

D.   AC Impedance Measurements

        For single sensor material samples, a 1.2"
platinum wire was connected to each of the electrodes

35      on the samples with stainless steel screws. The ends
of the platinum wires were then connected to 0.127"
diameter inconel wires that run to the exterior of the
test chamber. The entire lengths of the inconel wires

were encased in aluminum oxide and grounded inconel
tubing to eliminate interference from electromagnetic
fields present in the furnace.  The inconel tubes were
welded into a stainless steel flange that was mounted

5     on the end of a closed-one-end fused quartz reactor
that is 4" in diameter and 24" long.  The quartz
reactor was wrapped with grounded stainless steel
screen also to eliminate electromagnetic interference
from the furnace.  The entire chamber assembly was

10    placed in the cavity of a hinged Lindberg tube furnace
and the furnace was closed.

The samples were connected to the dielectric
interface (Solartron 1296) and frequency response
analyzer (Solartron 1260) using ten pairs of coaxial

15    cables (one pair per sample) which ran from the inconel
wires on the furnace exterior to a switch (Keithley
7001 containing two Keithley 7062 high frequency cards)
and one pair of coaxial cables from the switch to the
interface and analyzer.  The switch, dielectric

20    interface and frequency analyzer were all computer
controlled.

The gas flows into the quartz chamber were
regulated using a computer controlled system comprised
of 4 independent flowmeters (MKS product #1179) and

25    multi gas controller (MKS product #647B).  The
temperature of the furnace was determined using a
computer controlled fuzzy logic controller (Fuji PYX).

After the samples were loaded into the furnace,
the quartz reactor was purged with a synthetic air

30    mixture during heating of the furnace.  After the
furnace was equilibrated at the measurement
temperature, the gas concentrations ($N_2$, $O_2$, 1%CO/99%
$N_2$, and 1% $NO_2$/99% $N_2$ were set to the desired values
and sufficient time was allowed for the equilibration

35    of the atmosphere in the reactor.  At this point the AC
impedance measurements (1 Hz to 1 MHz) from each sample
were measured sequentially.  Then the gas
concentrations were typically set to a new value, the

atmosphere was equilibrated, and another round of
measurements were made.  The procedure was repeated
until the samples were measured in all of the desired
atmospheres at a particular temperature.  At this point
5    the temperature was changed and the process repeated.
After all of the measurements had been made the furnace
was cooled to room temperature and the samples removed.

       For the sensor array chips, a measurement system
similar to that described above can be used.  The only
10   difference is that the platinum wires, which are
connected to the inconel wires in the furnace, must be
connected to the electrode pads on the array chip using
a conducting paste (Pelco product #16023).  The number
of connections from the sample to the switch depends on
15   the number of sensors on the array.

Example 1

       This example shows the change in the electrical
properties of 20 metal oxide semiconducting materials
in the presence of 4 combustion gas compositions at
20   450°C.  The signals listed in Table 1 below are from
the infrared thermographic technique described above.
The signals represent differences in temperature (°C)
of the materials when exposed to one of the 4 gas
compositions shown relative to that in a comparison gas
25   which is 2% $O_2$/ 98% $N_2$ and reflect the change in the
electrical resistance of the semiconducting materials.
All of the signals were generated with 10 V across the
materials, unless otherwise specified.  Blank spaces
indicate that there was no detectable signal when that
30   gas composition was contacted with that material.
Unless otherwise specified, the gases were measured at
2000 ppm in $N_2$.

Table 1
35   Change in temperature in °C

| | ZnO | $SnO_2$ | $NiFe_2O_4$ | $WO_3$ | 1% $Nb:TiO_2$ | $Pr_6O_{11}$ | $SrNb_2O_6$ |
|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | -38.1 | -35.4 | -27.4 | -16.4 | -2.7 | -5.6 | -2.8 |
| $NO_2$ in 2% | -35.2 | -32.5 | -13.7 | -13.5 | -2.7 | - | - |

| $O_2$/ 98% $N_2$ | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO in $N_2$ | 27.2 | 8.2 | 14 | 13.7 | - | - | 8.3 |
| $N_2$ ref. | 16.9 | 9.6 | 11.2 | 5.6 | 12.4 | - | - |

| | NiO | CuO | $Cu_2O$ | $MnTiO_3$ | $BaCuO_{2.5}$ | $AlVO_4$ | $CuMnFeO_4$ |
|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 5.5 | 8.2 | 8.2 | 5.6 | 6.6 | - | - |
| $NO_2$ in 2% $O_2$/ 98% $N_2$ | 5.5 | 5.6 | 5.5 | - | 2.6 | -2.7 | 2.6 |
| CO in $N_2$ | - | -5.5 | -13.8 | - | -2.7 | 11.3 | - |
| $N_2$ ref. | -2.8 | -5.6 | -2.8 | - | -2.7 | 8.3 | - |

| | $LaFeO_3$ | $CuGaO_2$ | $CuFe_2O_4$ | $Zn_4TiO_6$ | $La_2CuO_4$ | $SrCu_2O_2$ |
|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | - | -2.8 | -5.5 | -5.7 | 4.2 | - |
| $NO_2$ in 2% $O_2$/ 98% $N_2$ | - | - | -2.5 | - | - | 2.6 |
| CO in $N_2$ | -2.8 | - | - | 7.3 | - | - |
| $N_2$ ref. | - | - | - | - | - | - |

The following measurements were done with other than 10 V. $Pr_6O_{11}$ was measured using 1 V; $BaCuO_{2.5}$, $CuMnFeO_4$, $CuGaO_2$ and $CuFe_2O4$ were measured using 16 V; $Zn_4TiO_6$ was measured using 20 V; $LaCuO_4$ and $SrCu_2O_2$ were measured using 12 V.

Example 2

This example shows the change in the electrical properties of 8 metal oxide semiconducting materials in the presence of 5 combustion gas compositions at 450°C. The signals listed in Table 2 below are from the infrared thermographic technique. The signals are differences in temperature (°C) of the semiconducting materials when exposed to the gas compositions shown relative to that in a comparison gas which is 2% $O_2$/ 98% $N_2$. All of the signals were generated with 10 V across the semiconducting materials, unless otherwise specified. Blank spaces indicate that there was no detectable signal when that gas composition was contacted with that material. Unless otherwise specified, the gases were measured at 2000 ppm in $N_2$.

Table 2

Change in temperature in °C

| | ZnO | SnO$_2$ | WO$_3$ | SrNb$_2$O$_6$ | NiO | CuO | Cu$_2$O | AlVO$_4$ |
|---|---|---|---|---|---|---|---|---|
| NO$_2$ in N$_2$ | -38.1 | -35.4 | -16.4 | -2.8 | 5.5 | 8.2 | 8.2 | - |
| NO$_2$ in 2% O$_2$/ 98% N$_2$ | -35.2 | -32.5 | -13.5 | - | 5.5 | 5.6 | 5.5 | -2.7 |
| CO in N$_2$ | 27.2 | 8.2 | 13.7 | 8.3 | | -5.5 | -13.8 | 11.3 |
| N$_2$ ref. | 16.9 | 9.6 | 5.6 | - | -2.8 | -5.6 | -2.8 | 8.3 |
| 1% C$_4$H$_{10}$/ 99% N$_2$ | 38 | 28 | 22 | | -6 | -7 | -11 | 11 |

Example 3

This example shows the change in the electrical properties of 26 metal oxide semiconducting materials in the presence of 4 combustion gas compositions at 600°C. The signals listed in Table 3 immediately below were obtained using an infrared thermographic technique. The signals are measurements of the differences in temperature (°C) of the materials when exposed to the gas compositions shown relative to that in a comparison gas which is 2% O$_2$/ 98% N$_2$. All of the signals were generated with 10 V across the materials, unless otherwise specified. Blank spaces indicate that there was no detectable signal when that gas composition was contacted with that material. Unless otherwise specified, the gases were measured at 2000 ppm in N$_2$.

Table 3
Change in temperature in °C

| | ZnO | SnO$_2$ | NiFe$_2$O$_4$ | 1% Nb:TiO$_2$ | WO$_3$ | FeTiO$_3$ | SrTiO$_3$ | NiO |
|---|---|---|---|---|---|---|---|---|
| NO$_2$ in N$_2$ | -54.4 | -48.3 | -36.3 | -24.2 | -18.1 | -6.1 | 3 | 6 |
| NO$_2$ in 2% O$_2$/ 98% N$_2$ | -48.3 | -48.3 | -30.2 | -12.1 | -18.1 | -6.1 | 6 | 6 |
| CO in N$_2$ | 28.5 | 18.1 | 18.5 | 42.3 | 24.1 | - | - | -6 |
| N$_2$ | 30.2 | 24.1 | 15.1 | 24.1 | 6 | 3 | - | -9.1 |

| | AlVO$_4$ | CuO | Cu$_2$O | LaFeO$_3$ | BaCuO$_{2.5}$ | Fe$_2$O$_3$ | SrNb$_2$O$_6$ | ZnO + 2.5% F2889 |
|---|---|---|---|---|---|---|---|---|

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | - | - | - | - | - | - | - | -24 |
| $NO_2$ in 2% $O_2$/ 98% $N_2$ | -6.1 | 6 | 6 | - | - | - | - | -18 |
| CO in $N_2$ | 18.1 | -6 | -12.1 | -3 | -6 | 72.5 | 28.5 | 18 |
| $N_2$ | 18.1 | -3 | - | - | -6 | - | 18.1 | 21 |

| | ZnO + 10% F3876 | $SnO_2$ + 5% F2889 | $WO_3$ + 10% F3876 | $CuFe_2O_4$ | $Zn_4TiO_6$ | $ZnTiO_3$ | $Tm_2O_3$ | $Yb_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | -42 | -6 | -15 | -6 | -12 | -6 | -6 | -6 |
| $NO_2$ in 2% $O_2$/ 98% $N_2$ | -24 | -6 | -18 | -6 | - | - | - | - |
| CO in $N_2$ | 12 | 24 | 6 | - | 6 | - | - | - |
| $N_2$ | 27 | 9 | 18 | - | 6 | - | - | - |

| | $Fe:ZrO_2$ | $MnCrO_3$ |
|---|---|---|
| $NO_2$ in $N_2$ | -6 | - |
| $NO_2$ in 2% $O_2$/ 98% $N_2$ | - | - |
| CO in $N_2$ | 6 | 24 |
| $N_2$ | - | - |

All of the measurements were obtained using 10 V, except that $BaCuO_{2.5}$ was measured with 4 V; $Fe_2O_3$ was measured with 1 V; ZnO + 2.5% F2889, ZnO + 10% F3876, $SnO_2$ + 5% F2889, $Tm_2O_3$, $Yb_2O_3$, $Fe:ZrO_2$ and $MnCrO_3$ were measured with 5 V; $WO_3$ + 10% F3876 was measured with 2 V; $CuFe_2O_4$ was measured with 6 V; and $Zn_4TiO_6$ and $ZnTiO_3$ were measured using 20 V.

Example 4

This example illustrates that a set of 4 metal oxide materials of Example 3 could be used to differentiate the 4 gas compositions shown at 600°C using the IR thermographic signals. The results are shown in Table 4 below. The signals are measurements of the differences in temperature (°C) of the materials when exposed to the gases shown relative to that in a

comparison gas which is 2% $O_2$/ 98% $N_2$. All of the
signals were generated with 10 V across the materials,
unless otherwise specified. Blank spaces indicate that
there was no detectable signal when that gas
composition was contacted with that material. Unless
otherwise specified, the gases were measured at
2000 ppm in $N_2$.

Table 4
Change in temperature in °C

| | $SrTiO_3$ | $Cu_2O$ | $Fe_2O_3$ | $SrNb_2O_6$ |
|---|---|---|---|---|
| $NO_2$ in $N_2$ | 3 | - | - | - |
| $NO_2$ in 2% $O_2$/ 98% $N_2$ | 6 | 6 | - | - |
| CO in $N_2$ | - | -12.1 | 72.5 | 28.5 |
| $N_2$ | - | - | - | 18.1 |

Example 5

This example demonstrates that this second set of
4 metal oxide materials of Example 3 could be used to
differentiate the 4 gas compositions shown at 600°C
using the IR thermographic signals. The results are
shown in Table 5 below. The signals are measurements
of the differences in temperature (°C) of the materials
when exposed to the gases shown relative to that in a
comparison gas which is 2% $O_2$/ 98% $N_2$. All of the
signals were generated with 10 V across the materials,
unless otherwise specified. Blank spaces indicate that
there was no detectable signal when that gas
composition was contacted with that material. Unless
otherwise specified, the gases were measured at
2000 ppm in $N_2$.

Table 5
Change in temperature in °C

| | ZnO | $AlVO_4$ | $LaFeO_3$ | $BaCuO_{2.5}$ |
|---|---|---|---|---|
| $NO_2$ in $N_2$ | -54.4 | - | - | - |
| $NO_2$ in 2% $O_2$/ 98% | -48.3 | -6.1 | - | - |

| N₂ | | | | |
|---|---|---|---|---|
| CO in N₂ | 28.5 | 18.1 | -3 | -6 |
| N₂ | 30.2 | 18.1 | - | -6 |

Comparative Example A

      This comparative example demonstrates that this set of 6 materials of Example 3 can not be used to
5    differentiate the 2 gas compositions at 600°C using the IR thermographic signals, and illustrates the importance of the proper selection of materials. The results are shown in Table 5A below. The signals are measurements of the differences in temperature (°C) of
10   the materials when exposed to the gas compositions shown relative to that in a comparison gas which is 2% $O_2$/ 98% $N_2$. All of the signals were generated with 10 V across the materials, unless otherwise specified. Blank spaces indicate that there was no detectable
15   signal when that gas composition was contacted with that material. Unless otherwise specified, the gases were measured at 2000 ppm in $N_2$.

<div align="center">

Table 5a

Change in temperature in °C

</div>

20

| | $SnO_2$ | $WO_3$ | $FeTiO_3$ | Ni O | $SnO_2$ + 5% F2889 | $CuFe_2O_4$ |
|---|---|---|---|---|---|---|
| NO₂ in N₂ | -48.3 | -18.1 | -6.1 | 6 | -6 | -6 |
| NO₂ in 2% O₂/ 98% N₂ | -48.3 | -18.1 | -6.1 | 6 | -6 | -6 |

Comparative Example B

      This comparative example demonstrates that this set of 3 materials can not be used to differentiate the
25   2 gas compositions at 600°C using the IR thermographic signals, and illustrates the importance of the proper selection of materials. The results are shown in Table 5B below. The signals are measurements of the differences in temperature (°C) of the materials when
30   exposed to the gas compositions shown relative to that

in a comparison gas which is 2% $O_2$/ 98% $N_2$. All of the signals were generated with 10 V across the materials, unless otherwise specified. Blank spaces indicate that there was no detectable signal when that gas composition was contacted with that material. Unless otherwise specified, the gases were measured at 2000 ppm in $N_2$.

Table 5b

Change in temperature in °C

|  | $AlVO_4$ | $BaCuO_{2.5}$ | $Zn_4TiO_6$ |
|---|---|---|---|
| CO in $N_2$ | 18.1 | -6 | 6 |
| $N_2$ | 18.1 | -6 | 6 |

Example 6

This example illustrates the use of the AC impedance technique for the measurement of the response of 19 metal oxide semiconducting materials in the presence of 4 gas compositions at 400°C. The signals listed in Table 6 below are the ratios of the magnitudes of the impedances of the materials when exposed to the gas compositions shown to the magnitudes of the impedances in 10,000 ppm $O_2$ in $N_2$. The gases used were 200 ppm $NO_2$ in $N_2$, 200 ppm $NO_2$ and 10,000 ppm $O_2$ in $N_2$, 1000 ppm CO in $N_2$, and $N_2$.

Table 6

|  | $MgAl_2O_4$ | 1% Zn:$MgAl_2O_4$ | ZnO | $WO_3$ | $NiFe_2O_4$ | $SnO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 0.6245 | 0.5544 | 55.85 | 8.772 | 5.008 | 9.243 | 1.536 |
| $NO_2$ in $O_2$/ $N_2$ | 0.7680 | 0.6787 | 47.38 | 9.468 | 12.93 | 10.56 | 1.585 |
| CO in $N_2$ | 1.531 | 1.459 | 0.1235 | 0.1865 | 1.248 | 0.0051 | 0.0116 |
| $N_2$ | 0.8242 | 0.9219 | 4.1290 | 1.716 | 1.327 | 0.3208 | 1.055 |

|  | $MnTiO_3$ | NiO | $SrNb_2O_6$ | $CeVO_4$ | 1% Nb:$TiO_2$ | $FeTiO_3$ | $Pr_6O_{11}$ |
|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 0.8643 | 0.5692 | 1.217 | 0.9847 | 1.937 | 1.299 | 0.5475 |
| $NO_2$ in $O_2$/ $N_2$ | 0.8475 | 0.9662 | 1.228 | 0.9977 | 1.674 | 1.034 | 0.5452 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CO in N$_2$ | 37.35 | 9.679 | 0.6501 | 1.045 | 0.0112 | 0.6009 | 1.184 |
| N$_2$ | 1.264 | 1.257 | 1.011 | 1.001 | 0.8811 | 1.028 | 1.103 |

| | SrTiO$_3$ | Ba$_2$Cu$_2$O$_5$ | CuMnFe$_2$O$_4$ | LaFeO$_3$ | Zn$_2$V$_2$O$_7$ |
|---|---|---|---|---|---|
| NO$_2$ in N$_2$ | 0.6524 | 0.7869 | 0.9559 | 0.8401 | 1.209 |
| NO$_2$ in O$_2$/ N$_2$ | 0.7596 | 0.7834 | 0.9399 | 0.8506 | 1.114 |
| CO in N$_2$ | 0.0178 | 0.7603 | 0.6089 | 2037 | 0.8529 |
| N$_2$ | 1.061 | 1.063 | 1.136 | 1.756 | 0.9900 |

Example 7

This example illustrates the use of the AC impedance technique for the measurement of the response of 19 metal oxide semiconducting materials in the presence of 4 gas compositions at 550°C. The signals listed in the table are from the AC impedance technique. The signals are the ratios of the magnitudes of the impedances of the materials when exposed to the gas compositions shown to the magnitudes of the impedances in 10,000 ppm O$_2$ in N$_2$. The gases used were 200 ppm NO$_2$ in N$_2$, 200 ppm NO$_2$ & 10,000 ppm O$_2$ in N$_2$, 1000 ppm CO in N$_2$, and N$_2$.

Table 7

| | MgAl$_2$O$_4$ | 1% Zn:MgAl$_2$O$_4$ | ZnO | WO$_3$ | NiFe$_2$O$_4$ | SnO$_2$ |
|---|---|---|---|---|---|---|
| NO$_2$ in N$_2$ | 0.9894 | 0.9583 | 3.866 | 2.335 | 3.025 | 1.655 |
| NO$_2$ in O$_2$/ N$_2$ | 0.8937 | 0.8984 | 5.272 | 2.006 | 3.553 | 3.390 |
| CO in N$_2$ | 1.046 | 0.9697 | 0.0133 | 0.2034 | 0.2506 | 0.0069 |
| N$_2$ | 1.067 | 1.060 | 0.7285 | 0.9526 | 1.208 | 0.2666 |

| | TiO$_2$ | MnTiO$_3$ | NiO | SrNb$_2$O$_6$ | CeVO$_4$ | 1% Nb:TiO$_2$ | FeTiO$_3$ |
|---|---|---|---|---|---|---|---|
| NO$_2$ in N$_2$ | 1.135 | 1.010 | 0.9483 | 1.006 | 1.003 | 1.271 | 1.193 |
| NO$_2$ in O$_2$/ N$_2$ | 1.314 | 1.014 | 0.5207 | 1.044 | 0.9975 | 1.302 | 1.073 |
| CO in N$_2$ | 0.0017 | 44.00 | 1.194 | 0.2814 | 1.104 | 0.0021 | 0.6743 |
| N$_2$ | 0.7263 | 1.280 | 1.341 | 0.9830 | 1.024 | 0.477 | 1.054 |

| | $Pr_6O_{11}$ | $SrTiO_3$ | $Ba_2Cu_2O_5$ | $CuMnFe_2O_4$ | $LaFeO_3$ | $Zn_2V_2O_7$ |
|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 1.223 | 0.9055 | 0.7071 | 1.148 | 1.302 | 1.199 |
| $NO_2$ in $O_2/N_2$ | 0.9656 | 0.9881 | 0.3812 | 0.9891 | 0.9429 | 1.086 |
| CO in $N_2$ | 62.76 | 0.0029 | 3.0892 | 2.557 | 123.3 | 0.4726 |
| $N_2$ | 1.495 | 1.210 | 1.333 | 1.681 | 1.789 | 0.9034 |

Example 8

This example illustrates the use of the AC impedance technique for the measurement of the response of 23 semiconducting materials in the presence of 4 gas compositions at 650-700°C. The signals listed in the table are from the AC impedance technique. The signals are the ratios of the magnitudes of the impedances of the materials when exposed to the gas compositions shown to the magnitudes of the impedances in 10,000 ppm $O_2$ in $N_2$. The gases used were 200 ppm $NO_2$ in $N_2$, 200 ppm $NO_2$ & 10,000 ppm $O_2$ in $N_2$, 1000 ppm CO in $N_2$, and $N_2$.

Table 8

| | $MgAl_2O_4$ | 1% $Zn:MgAl_2O_4$ | ZnO | $WO_3$ | $NiFe_2O_4$ | $SnO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 0.9450 | 1.022 | 0.4876 | 0.7151 | 0.5807 | 0.5419 | 0.5617 |
| $NO_2$ in $O_2/N_2$ | 0.6412 | 0.8310 | 1.235 | 1.281 | 1.105 | 0.8265 | 1.030 |
| CO in $N_2$ | 0.9074 | 0.9684 | 0.0348 | 0.2693 | 0.0408 | 0.0238 | 0.0015 |
| $N_2$ | 1.056 | 1.100 | 0.2753 | 0.6332 | 0.4421 | 0.3521 | 0.3957 |

| | $MnTiO_3$ | NiO | $SrNb_2O_6$ | $CeVO_4$ | 1% $Nb:TiO_2$ | $FeTiO_3$ | $Pr_6O_{11}$ |
|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 1.445 | 1.379 | 0.8852 | 1.050 | 0.5711 | 0.9072 | 1.516 |
| $NO_2$ in $O_2/N_2$ | 0.9561 | 0.8127 | 0.9862 | 1.135 | 0.8263 | 0.9524 | 0.9814 |
| CO in $N_2$ | 113.3 | 1.782 | 0.0301 | 1.565 | 0.0035 | 0.4346 | 8005 |
| $N_2$ | 1.877 | 1.409 | 0.8788 | 1.080 | 0.2802 | 0.8050 | 1.962 |

| | $SrTiO_3$ | $Ba_2Cu_2O_5$ | $CuMnFe_2O_4$ | $LaFeO_3$ | $Zn_2V_2O_7$ |
|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 1.051 | 0.5615 | 3.401 | 1.331 | 0.8631 |
| $NO_2$ in $O_2/N_2$ | 0.9320 | 0.9703 | 1.001 | 1.013 | 0.9459 |

| | | | | | |
|---|---|---|---|---|---|
| $O_2/N_2$ | | | | | |
| CO in $N_2$ | 0.0020 | 381.3 | 2.198 | 43.11 | 0.4672 |
| $N_2$ | 1.076 | 1.308 | 4.250 | 1.673 | 0.6574 |

| | ZnO + 2.5% F2889 | ZnO + 10% F3876 | $SnO_2$ + 5% F2889 | $WO_3$ + 10% F3876 |
|---|---|---|---|---|
| $NO_2$ in $N_2$ | 0.5810 | 0.7944 | 0.6270 | 0.6055 |
| $NO_2$ in $O_2/N_2$ | 1.141 | 1.176 | 0.8927 | 1.284 |
| CO in $N_2$ | 0.0020 | 0.0016 | 0.0043 | 0.0122 |
| $N_2$ | 0.1054 | 0.1338 | 0.2780 | 0.4862 |

Example 9

This example illustrates the use of the AC impedance technique for the measurement of the response of 16 semiconducting materials in the presence of 4 gas compositions at 800°C. The signals listed in the table are from the AC impedance technique. The signals are the ratios of the magnitudes of the impedances of the materials when exposed to the gas compositions shown to the magnitudes of the impedances in 10,000 ppm $O_2$ in $N_2$. The gases used were 200 ppm $NO_2$ in $N_2$, 200 ppm $NO_2$ & 10,000 ppm $O_2$ in $N_2$, 1000 ppm CO in $N_2$, and $N_2$.

Table 9

| | ZnO | $WO_3$ | $NiFe_2O_4$ | $SnO_2$ | $TiO_2$ | $MnTiO_3$ | NiO | $SrNb_2O_6$ |
|---|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 0.3980 | 0.5737 | 0.6710 | 0.4050 | 0.4859 | 1.981 | 1.917 | 0.7555 |
| $NO_2$ in $O_2/N_2$ | 1.594 | 1.117 | 4.795 | 6.456 | 1.052 | 1.497 | 0.8529 | 0.9928 |
| CO in $N_2$ | 0.688 | 0.2610 | 0.0642 | 0.2349 | 0.0014 | 123.2 | 5.129 | 0.0144 |
| $N_2$ | 0.3070 | 0.5103 | 0.5339 | 0.2852 | 0.3093 | 2.882 | 2.124 | 0.5167 |

| | $CeVO_4$ | 1% $Nb:TiO_2$ | $FeTiO_3$ | $Pr_6O_{11}$ | $SrTiO_3$ | $Ba_2Cu_2O_5$ | $CuMnFe_2O_4$ | $LaFeO_3$ |
|---|---|---|---|---|---|---|---|---|
| $NO_2$ in $N_2$ | 1.013 | 0.3280 | 0.6799 | 1.569 | 0.0049 | 4.061 | 2.869 | 1.252 |
| $NO_2$ in $O_2/N_2$ | 1.058 | 1.006 | 0.9982 | 1.010 | 0.0260 | 0.9811 | 0.9389 | 1.326 |
| CO in $N_2$ | 2.165 | 0.0047 | 0.2831 | 3530 | 1.004 | 216.0 | 0.8810 | 63.36 |
| $N_2$ | 1.075 | 0.1960 | 0.5600 | 2.999 | 1.048 | 7.445 | 3.413 | 1.612 |

CLAIMS

What is claimed is:

1. An apparatus for analyzing at least one individual gas component in a multi-component gas mixture, comprising:

(a)    an array of at least two chemo/electro-active materials connected in parallel circuitry, each chemo/electro-active material exhibiting a different electrical response characteristic upon exposure to the individual gas component than each other chemo/electro-active material;

(b)    means for determining an electrical response of each chemo/electro-active material upon exposure of the array to the gas mixture;

(c)    means for determining a value for the temperature of the array connected in parallel circuitry with the chemo/elctro-active materials;  and

(d)    means for digitizing the electrical responses and the temperature value, and calculating a value from the digitized electrical responses and temperature value, to perform an analysis of the individual gas component.

2. An apparatus according to Claim 1 wherein the array is situated within the gas mixture, which has a temperature of about 400°C or more.

3. An apparatus according to Claim 1 wherein the gas mixture is an emission from a combustion process.

4. An apparatus according to Claim 1 wherein the component gases in the gas mixture are not separated.

5. An apparatus according to Claim 1 wherein the temperature of each chemo/electro-active material is determined substantially only by the variable temperature of the gas mixture.

6. An apparatus according to Claim 1 wherein the analysis is performed from the electrical responses of the chemo/electro-active materials upon exposure to the multi-component gas mixture only.

7. An apparatus according to Claim 1 wherein the means for performing analysis is means for calculating the concentration within the gas mixture of the individual gas component.

8. An apparatus according to Claim 1 wherein at least one chemo/electro-active material, when at a temperature of about 400°C or more, (i) has an electrical resistivity in the range of about 1 ohm-cm to about $10^5$ ohm-cm, and (ii) exhibits a change in electrical resistance of at least about 0.1 percent upon exposure of the material to an individual gas component, as compared to the resistance before exposure.

9. An apparatus according to Claim 1 wherein the electrical response characteristic of each material upon exposure to the gas mixture at a selected temperature is quantifiable as a value, and the response value of at least one material is constant or varies by no more than about twenty percent during exposure of the material to an individual gas component at the selected temperature for a period of at least about one minute.

10. An apparatus according to Claim 1 wherein the electrical response is selected from the group consisting of resistance, impedance, capacitance, voltage or current.

11. An apparatus according to Claim 1 wherein at least one chemo/electro-active material is a metal oxide.

12. In a multi-component gas mixture having a temperature of about 400°C or more, an apparatus for calculating the concentration of at least two individual analyte gas components in the mixture, comprising:

(a)     an array of at least three chemo/electro-
        active materials, the array being situated
        within the gas mixture, and each
        chemo/electro-active material having a
5       different electrical response
        characteristic upon exposure to each of
        the individual analyte gas components than
        each of the other chemo/electro-active
        materials;

10      (b)     means for determining an electrical
        response of each chemo/electro-active
        material upon exposure of the array to the
        unseparated components of the gas mixture;
        and

15      (c)     means for calculating the concentration of
        each of the individual analyte gas
        components from the electrical responses
        of the chemo/electro-active materials upon
        exposure to the multi-component gas

20      mixture only.

    13. An apparatus according to Claim 12 wherein the
gas mixture is an emission from a combustion process.

    14. An apparatus according to Claim 12 wherein the
temperature of each chemo/electro-active material is
25  determined substantially only by the variable
temperature of the gas mixture.

    15. An apparatus according to Claim 12 wherein at
least one chemo/electro-active material, when at a
temperature of about 400°C or more, (i) has an
30  electrical resistivity in the range of about 1 ohm-cm
to about $10^5$ ohm-cm, and (ii) exhibits a change in
electrical resistance of at least about 0.1 percent
upon exposure of the material to an analyte gas
component, as compared to the resistance before
35  exposure

    16. An apparatus according to Claim 12 wherein the
electrical response characteristic of each material
upon exposure to the gas mixture at a selected

temperature is quantifiable as a value, and the
response value of at least one material is constant or
varies by no more than about twenty percent during
exposure of the material to an analyte gas component at
5      the selected temperature for a period of at least about
one minute.

17. An apparatus according to Claim 12 wherein the
electrical response is selected from the group
consisting of resistance, impedance, capacitance,
10     voltage or current.

18. An apparatus according to Claim 12 wherein at
least one chemo/electro-active material is a metal
oxide.

19. In a multi-component gas mixture having a
15     temperature of about 400°C or more, an apparatus for
calculating the concentration of at least two
individual analyte gas components in the mixture,
comprising:

        (a)   an array of at least three chemo/electro-
20                  active materials connected in parallel
             circuitry, the array being situated within
             the gas mixture, and each chemo/electro-
             active material exhibiting a change in
             electrical resistance upon exposure to
25                  each of the individual analyte gas
             components, wherein at least one
             chemo/electro-active material, when at a
             temperature of about 400°C or more, (i)
             has an electrical resistivity in the range
30                  of  about 1 ohm-cm to about  $10^5$ ohm-cm,
             and (ii) exhibits a change in electrical
             resistance of at least about 0.1 percent
             upon exposure of the material to an
             analyte gas component, as compared to the
35                  resistance before exposure;
        (b)   means for determining the change in
             resistance of each chemo/electro-active

material upon exposure of the array to the
gas mixture; and

    (c)    means for calculating the concentration of
each of the individual analyte gas
components from the changes in resistance
of the chemo/electro-active materials.

20. An apparatus according to Claim 19 wherein the
gas mixture is an emission from a combustion process.

21. An apparatus according to Claim 19 wherein the
temperature of each chemo/electro-active material is
determined substantially only by the variable
temperature of the gas mixture.

22. An apparatus according to Claim 19 wherein the
electrical response characteristic of each material
upon exposure to the gas mixture at a selected
temperature is quantifiable as a value, and the
response value of at least one material is constant or
varies by no more than about twenty percent during
exposure of the material to an analyte gas component at
the selected temperature for a period of at least about
one minute.

23. An apparatus according to Claim 19 wherein at
least one chemo/electro-active material is a metal
oxide.

24. An apparatus for analyzing at least one
individual gas component in a multi-component gas
mixture, comprising:

    (a)    an array of at least two chemo/electro-
active materials, each chemo/electro-
active material having a different
electrical response characteristic upon
exposure at a selected temperature to the
individual gas component than each of the
other chemo/electro-active materials, the
electrical response characteristic of each
material being quantifiable as a value,
wherein the response value of at least one
material is constant or varies by no more

than about twenty percent during exposure
of the material to an individual gas
component at the selected temperature for
a period of at least about one minute;

5          (b)    means for determining the electrical
response value of each chemo/electro-
active material upon exposure of the array
to the gas mixture;    and

           (c)    means for performing an analysis of the
10                 individual gas component from the
electrical response values.

           25. An apparatus according to Claim 24 wherein the
array is situated within the gas mixture, which has a
temperature of about 400°C or more.

15         26. An apparatus according to Claim 24 wherein the
gas mixture is an emission from a combustion process.

           27. An apparatus according to Claim 24 wherein the
means for performing analysis is means for calculating
the concentration within the gas mixture of the
20  individual gas component.

           28. An apparatus according to Claim 24 wherein the
temperature of each chemo/electro-active material is
determined substantially only by the variable
temperature of the gas mixture.

25         29. An apparatus according to Claim 24 wherein the
electrical response is selected from the group
consisting of resistance, impedance, capacitance,
voltage or current.

           30. An apparatus according to Claim 24 wherein at
30  least one chemo/electro-active material is a metal
oxide.

           31. In a multi-component gas mixture having a
temperature of less than about 400°C, an apparatus for
analyzing at least one individual gas component in the
35  mixture, comprising:

           (a)    an array of at least two chemo/electro-
active materials, each chemo/electro-
active material having a different

electrical response characteristic upon
exposure at a selected temperature to the
individual gas component than each of the
other chemo/electro-active materials, the
array being situated within the gas
mixture, and having a substantially
constant temperature of about 400C or
more;

(b)    means for determining the electrical
       response value of each chemo/electro-
       active material upon exposure of the array
       to the gas mixture;  and

(c)    means for performing an analysis of the
       individual gas component from the
       electrical response values.

32. An apparatus according to Claim 31 wherein the
component gases in the gas mixture are not separated.

33. An apparatus according to Claim 31 wherein the
analysis is performed from the electrical responses of
the chemo/electro-active materials upon exposure to the
multi-component gas mixture only.

34. An apparatus according to Claim 31 wherein the
means for performing analysis is means for calculating
the concentration within the gas mixture of the
individual gas component.

35. An apparatus according to Claim 31 further
comprising means for determining a value for the
temperature of the gas mixture connected in parallel
circuitry with the chemo/elctro-active materials, and
wherein the individual gas component is analyzed from
digitized electrical responses and a digitized
temperature value.

36. An apparatus according to Claim 31 wherein at
least one chemo/electro-active material, when at a
temperature of about 400°C or more, (i) has an
electrical resistivity in the range of about 1 ohm-cm
to about  $10^5$ ohm-cm, and (ii) exhibits a change in
electrical resistance of at least about 0.1 percent

upon exposure of the material to an individual gas component, as compared to the resistance before exposure.

37. An apparatus according to Claim 31 wherein the electrical response characteristic of each material upon exposure to the gas mixture at a selected temperature is quantifiable as a value, and the response value of at least one material is constant or varies by no more than about twenty percent during exposure of the material to an individual gas component at the selected temperature for a period of at least about one minute.

38. An apparatus according to Claim 31 wherein the electrical response is selected from the group consisting of resistance, impedance, capacitance, voltage or current.

39. An apparatus according to Claim 31 wherein at least one chemo/electro-active material is a metal oxide.

40. An apparatus for analyzing at least one individual gas component in a multi-component gas mixture, comprising:

    (a)   an array of first and second chemo/electro-active materials, each chemo/electro-active material having a different electrical response characteristic upon exposure at a selected temperature to the individual gas component than each of the other chemo/electro-active materials, wherein the chemo/electro-active materials are selected from the pairings in the group consisting of

    (i) the first material is $M^1O_x$, and the second material is $M^1_aM^2_bO_x$;

    (ii) the first material is $M^1O_x$, and the second material is $M^1_aM^2_bM^3_cO_x$;

51

(iii) the first material is $M^1{}_aM^2{}_bO_x$, and the second material is $M^1{}_aM^2{}_bM^3{}_cO_x$;

(iv) the first material is a first $M^1O_x$, and the second material is a second $M^1O_x$;

(v) the first material is a first $M^1{}_aM^2{}_bO_x$, and the second material is a second $M^1{}_aM^2{}_bO_x$; and

(vi) the first material is a first $M^1{}_aM^2{}_bM^3{}_cO_x$, and the second material is a second $M^1{}_aM^2{}_bM^3{}_cO_x$;

wherein $M^1$ is selected from the group consisting of Ce, Co, Cu, Fe, Ga, Nb, Ni, Pr, Ru, Sn, Ti, Tm, W, Yb, Zn, and Zr; $M^2$ and $M^3$ are each independently selected from the group consisting of Al, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Ru, Sb, Sc, Si, Sn, Sr, Ta, Ti, Tm, V, W, Y, Yb, Zn, and Zr, but $M^2$ and $M^3$ are not the same in $M^1{}_aM^2{}_bM^3{}_cO_x$; a, b and c are each independently about 0.0005 to about 1, provided that a+b+c = 1; and x is a number sufficient so that the oxygen present balances the charges of the other elements in the compound;

(b) means for determining the electrical response of each chemo/electro-active material upon exposure of the array to the gas mixture; and

(c) means for performing an analysis of the individual gas component from the electrical responses.

41. An apparatus according to Claim 40 wherein

(a) $M^1O_x$ is selected from the group consisting of $Ce_aO_x$, $CoO_x$, $CuO_x$, $FeO_x$, $GaO_x$, $NbO_x$, $NiO_x$, $PrO_x$, $RuO_x$, $SnO_x$, $Ta_aO_x$, $TiO_x$, $TmO_x$, $WO_x$, $YbO_x$, $ZnO_x$, $ZrO_x$, $SnO_x$ with Ag additive, $ZnO_x$ with Ag additive, $TiO_x$ with Pt additive, $ZnO_x$ with frit additive, $NiO_x$ with frit additive, $SnO_x$ with frit additive, or $WO_x$ with frit additive;

(b)   $M^1_aM^2_bO_x$ is selected from the group consisting of $Al_aCr_bO_x$, $Al_aFe_bO_x$, $Al_aMg_bO_x$, $Al_aNi_bO_x$, $Al_aTi_bO_x$, $Al_aV_bO_x$, $Ba_aCu_bO_x$, $Ba_aSn_bO_x$, $Ba_aZn_bO_x$, $Bi_aRu_bO_x$, $Bi_aSn_bO_x$, $Bi_aZn_bO_x$, $Ca_aSn_bO_x$, $Ca_aZn_bO_x$, $Cd_aSn_bO_x$, $Cd_aZn_bO_x$, $Ce_aFe_bO_x$, $Ce_aNb_bO_x$, $Ce_aTi_bO_x$, $Ce_aV_bO_x$, $Co_aCu_bO_x$, $Co_aGe_bO_x$, $Co_aLa_bO_x$, $Co_aMg_bO_x$, $Co_aNb_bO_x$, $Co_aPb_bO_x$, $Co_aSn_bO_x$, $Co_aV_bO_x$, $Co_aW_bO_x$, $Co_aZn_bO_x$, $Cr_aCu_bO_x$, $Cr_aLa_bO_x$, $Cr_aMn_bO_x$, $Cr_aNi_bO_x$, $Cr_aSi_bO_x$, $Cr_aTi_bO_x$, $Cr_aY_bO_x$, $Cr_aZn_bO_x$, $Cu_aFe_bO_x$, $Cu_aGa_bO_x$, $Cu_aLa_bO_x$, $Cu_aNa_bO_x$, $Cu_aNi_bO_x$, $Cu_aPb_bO_x$, $Cu_aSn_bO_x$, $Cu_aSr_bO_x$, $Cu_aTi_bO_x$, $Cu_aZn_bO_x$, $Cu_aZr_bO_x$, $Fe_aGa_bO_x$, $Fe_aLa_bO_x$, $Fe_aMo_bO_x$, $Fe_aNb_bO_x$, $Fe_aNi_bO_x$, $Fe_aSn_bO_x$, $Fe_aTi_bO_x$, $Fe_aW_bO_x$, $Fe_aZn_bO_x$, $Fe_aZr_bO_x$, $Ga_aLa_bO_x$, $Ga_aSn_bO_x$, $Ge_aNb_bO_x$, $Ge_aTi_bO_x$, $In_aSn_bO_x$, $K_aNb_bO_x$, $Mn_aNb_bO_x$, $Mn_aSn_bO_x$, $Mn_aTi_bO_x$, $Mn_aY_bO_x$, $Mn_aZn_bO_x$, $Mo_aPb_bO_x$, $Mo_aRb_bO_x$, $Mo_aSn_bO_x$, $Mo_aTi_bO_x$, $Mo_aZn_bO_x$, $Nb_aNi_bO_x$, $Nb_aNi_bO_x$, $Nb_aSr_bO_x$, $Nb_aTi_bO_x$, $Nb_aW_bO_x$, $Nb_aZr_bO_x$, $Ni_aSi_bO_x$, $Ni_aSn_bO_x$, $Ni_aY_bO_x$, $Ni_aZn_bO_x$, $Ni_aZr_bO_x$, $Pb_aSn_bO_x$, $Pb_aZn_bO_x$, $Rb_aW_bO_x$, $Ru_aSn_bO_x$, $Ru_aW_bO_x$, $Ru_aZn_bO_x$, $Sb_aSn_bO_x$, $Sb_aZn_bO_x$, $Sc_aZr_bO_x$, $Si_aSn_bO_x$, $Si_aTi_bO_x$, $Si_aW_bO_x$, $Si_aZn_bO_x$, $Sn_aTa_bO_x$, $Sn_aTi_bO_x$, $Sn_aW_bO_x$, $Sn_aZn_bO_x$, $Sn_aZr_bO_x$, $Sr_aTi_bO_x$, $Ta_aTi_bO_x$, $Ta_aZn_bO_x$, $Ta_aZr_bO_x$, $Ti_aV_bO_x$, $Ti_aW_bO_x$, $Ti_aZn_bO_x$, $Ti_aZr_bO_x$, $V_aZn_bO_x$, $V_aZr_bO_x$, $W_aZn_bO_x$, $W_aZr_bO_x$, $Y_aZr_bO_x$, $Zn_aZr_bO_x$, $Al_aNi_bO_x$ with frit additive, $Cr_aTi_bO_x$ with frit additive, $Fe_aNi_bO_x$ with frit additive, $Fe_aTi_bO_x$ with frit additive, $Nb_aTi_bO_x$ with frit additive, $Nb_aW_bO_x$ with frit additive, $Ni_aZn_bO_x$ with frit additive, $Ni_aZr_bO_x$ with frit additive, or $Ta_aTi_bO_x$ with frit additive; and/or

(c)   $M^1_aM^2_bM^3_cO_x$ is selected from the group consisting of $Al_aMg_bZn_cO_x$, $Al_aSi_bV_cO_x$, $Ba_aCu_bTi_cO_x$, $Ca_aCe_bZr_cO_x$, $Co_aNi_bTi_cO_x$,

$Co_aNi_bZr_cO_x$, $Co_aPb_bSn_cO_x$, $Co_aPb_bZn_cO_x$,
$Cr_aSr_bTi_cO_x$, $Cu_aFe_bMn_cO_x$, $Cu_aLa_bSr_cO_x$,
$Fe_aNb_bTi_cO_x$, $Fe_aPb_bZn_cO_x$, $Fe_aSr_bTi_cO_x$,
$Fe_aTa_bTi_cO_x$, $Fe_aW_bZr_cO_x$, $Ga_aTi_bZn_cO_x$,
$La_aMn_bNa_cO_x$, $La_aMn_bSr_cO_x$, $Mn_aSr_bTi_cO_x$,
$Mo_aPb_bZn_cO_x$, $Nb_aSr_bTi_cO_x$, $Nb_aSr_bW_cO_x$,
$Nb_aTi_bZn_cO_x$, $Ni_aSr_bTi_cO_x$, $Sn_aW_bZn_cO_x$,
$Sr_aTi_bV_cO_x$, $Sr_aTi_bZn_cO_x$, or $Ti_aW_bZr_cO_x$.

42. An apparatus according to Claim 40 wherein the array is situated within the gas mixture, which has a temperature of about 400°C or more.

43. An apparatus according to Claim 40 wherein the gas mixture is an emission from a combustion process.

44. An apparatus according to Claim 40 wherein the component gases in the gas mixture are not separated.

45. An apparatus according to Claim 40 wherein the analysis is performed from the electrical responses of the chemo/electro-active materials upon exposure to the multi-component gas mixture only.

46. An apparatus according to Claim 40 wherein the means for performing analysis is means for calculating the concentration within the gas mixture of the individual gas component.

47. An apparatus according to Claim 40 further comprising means for determining a value for the temperature of the gas mixture connected in parallel circuitry with the chemo/elctro-active materials, and wherein the individual gas component is analyzed from digitized electrical responses and a digitized temperature value.

48. An apparatus according to Claim 40 wherein the temperature of each chemo/electro-active material is determined substantially only by the variable temperature of the gas mixture.

49. An apparatus according to Claim 40 wherein at least one chemo/electro-active material, when at a temperature of about 400°C or more, (i) has an electrical resistivity in the range of about 1 ohm-cm

54

to about 10⁵ ohm-cm, and (ii) exhibits a change in electrical resistance of at least about 0.1 percent upon exposure of the material to an individual gas component, as compared to the resistance before
5    exposure.

50. An apparatus according to Claim 40 wherein the electrical response characteristic of each material upon exposure to the gas mixture at a selected temperature is quantifiable as a value, and the
10   response value of at least one material is constant or varies by no more than about twenty percent during exposure of the material to an individual gas component at the selected temperature for a period of at least about one minute.

15   51. An apparatus according to Claim 40 wherein the electrical response is selected from the group consisting of resistance, impedance, capacitance, voltage or current.

52. An apparatus for analyzing at least one
20   individual gas component in a multi-component gas mixture, comprising:

(a)    an array of at least two chemo/electro-active materials connected in parallel circuitry, each chemo/electro-active
25             material having a different electrical response characteristic upon exposure at a selected temperature to the individual gas component than each of the other chemo/electro-active materials, the
30             electrical response characteristic of each material being quantifiable as a value, wherein the response value of at least one material is constant or varies by no more than about twenty percent during exposure
35             of the material to an individual gas component at the selected temperature for a period of at least about one minute;

          (b)    means for determining the electrical
response value of each chemo/electro-
active material upon exposure of the array
to the gas mixture;

5       (c)    means for determining a value for the
temperature of the gas mixture connected
in parallel with the chemo/elctro-active
materials; and

          (d)    means for digitizing the electrical

10               responses and the temperature value, and
calculating a value from the digitized
electrical response and temperature value,
to perform an analysis of the individual
gas component.

15     53. An apparatus according to Claim 52 wherein the
array is situated within the gas mixture, which has a
temperature of about 400°C or more.

    54. An apparatus according to Claim 52 wherein the
gas mixture is an emission from a combustion process.

20     55. An apparatus according to Claim 52 wherein the
component gases in the gas mixture are not separated.

    56. An apparatus according to Claim 52 wherein the
temperature of each chemo/electro-active material is
determined substantially only by the variable

25 temperature of the gas mixture.

    57. An apparatus according to Claim 52 wherein the
analysis is performed from the electrical responses of
the chemo/electro-active materials upon exposure to the
multi-component gas mixture only.

30     58. An apparatus according to Claim 52 wherein the
means for performing analysis is means for calculating
the concentration within the gas mixture of the
individual gas component.

    59. An apparatus according to Claim 52 wherein at

35 least one chemo/electro-active material, when at a
temperature of about 400°C or more, (i) has an
electrical resistivity in the range of about 1 ohm-cm
to about $10^5$ ohm-cm, and (ii) exhibits a change in

electrical resistance of at least about 0.1 percent
upon exposure of the material to an individual gas
component, as compared to the resistance before
exposure.

5    60. An apparatus according to Claim 52 wherein the
electrical response is selected from the group
consisting of resistance, impedance, capacitance,
voltage or current.

61. An apparatus according to Claim 52 wherein the
10   array is situated within the gas mixture, which has a
temperature of less than about 400°C, and the array has
a substantially constant temperature of about 400°C or
more.

62. An apparatus according to Claim 52 wherein at
15   least one chemo/electro-active material is a metal
oxide.

63. In a multi-component gas mixture having a
temperature of about 400°C or more, an apparatus for
calculating the concentration of at least two
20   individual analyte gas components in the mixture,
comprising:

(a)   an array of at least three chemo/electro-
active materials connected in parallel
circuitry, the array being situated within
25                the gas mixture, and each chemo/electro-
active material exhibiting a change in
electrical resistance upon exposure to
each of the individual analyte gas
components, wherein at least one
30                chemo/electro-active material, when at a
temperature of about 400C or more, (i) has
an electrical resistivity in the range of
about 1 ohm-cm to about $10^5$ ohm-cm, and
(ii) exhibits a change in electrical
35                resistance of at least about 0.1 percent
upon exposure of the material to an
analyte gas component, as compared to the
resistance before exposure;

(b)     means for determining the change in
resistance of each chemo/electro-active
material upon exposure of the array to the
unseparated components of the gas mixture;
5               and

(c)     means for calculating the concentration of
each of the individual analyte gas
components from the changes in resistance
of the chemo/electro-active materials upon
10              exposure to the multi-component gas
mixture only.

64. An apparatus according to Claim 63 wherein the
gas mixture is an emission from a combustion process.

65. An apparatus according to Claim 63 further
15  comprising means for determining a value for the
temperature of the gas mixture connected in parallel
circuitry with the chemo/elctro-active materials, and
wherein the individual gas component is analyzed from
digitized electrical responses and a digitized
20  temperature value.

66. An apparatus according to Claim 63 wherein the
temperature of each chemo/electro-active material is
determined substantially only by the variable
temperature of the gas mixture.

25      67. An apparatus according to Claim 63 wherein the
electrical response characteristic of each material
upon exposure to the gas mixture at a selected
temperature is quantifiable as a value, and the
response value of at least one material is constant or
30  varies by no more than about twenty percent during
exposure of the material to an analyte gas component at
the selected temperature for a period of at least about
one minute.

68. An apparatus according to Claim 63 wherein at
35  least one chemo/electro-active material is a metal
oxide.

69. A method for analyzing at least one individual
gas component in a multi-component gas mixture,
comprising:

    (a)    providing an array of at least two
chemo/electro-active materials connected
in parallel circuitry, each chemo/electro-
active material exhibiting a different
electrical response characteristic upon
exposure to the individual gas component
than each other chemo/electro-active
material;

    (b)    exposing the array to the gas mixture ;

    (c)    determining an electrical response of each
chemo/electro-active material upon
exposure of the array to the gas mixture;

    (d)    determining a value for the temperature of
the gas mixture independently of the
determination of the electrical responses
of the chemo/elctro-active materials;  and

    (e)    digitizing the electrical responses and
the temperature value, and calculating a
value from the digitized electrical
responses and temperature value to perform
an analysis of the individual gas
component.

70. A method according to Claim 69 wherein the
array is situated within the gas mixture, which has a
temperature of about 400°C or more.

71. A method according to Claim 69 wherein the gas
mixture is an emission from a combustion process.

72. A method according to Claim 69 wherein the
component gases in the gas mixture are not separated.

73. A method according to Claim 69 wherein the
temperature of each chemo/electro-active material is
determined substantially only by the variable
temperature of the gas mixture.

74. A method according to Claim 69 wherein the
analysis is performed from the electrical responses of

the chemo/electro-active materials upon exposure to the
multi-component gas mixture only.

75. A method according to Claim 69 wherein the
analysis performed comprises calculating the
concentration within the gas mixture of the individual
gas component.

76. A method according to Claim 69 wherein at least
one chemo/electro-active material, when at a
temperature of about 400°C or more, (i) has an
electrical resistivity in the range of about 1 ohm-cm
to about $10^5$ ohm-cm, and (ii) exhibits a change in
electrical resistance of at least about 0.1 percent
upon exposure of the material to an individual gas
component, as compared to the resistance before
exposure.

77. A method according to Claim 69 wherein the
electrical response characteristic of each material
upon exposure to the gas mixture at a selected
temperature is quantifiable as a value, and the
response value of at least one material is constant or
varies by no more than about twenty percent during
exposure of the material to an individual gas component
at the selected temperature for a period of at least
about one minute.

78. A method according to Claim 69 wherein the
electrical response is selected from the group
consisting of resistance, impedance, capacitance,
voltage or current.

79. A method according to Claim 69 wherein the
array is situated in the gas mixture, which has a
temperature of less than about 400°C, and the array has
a substantially constant temperature of about 400C or
more.

80. A method according to Claim 69 wherein at least
one chemo/electro-active material is a metal oxide.

81. A method for calculating the concentration of
at least two individual analyte gas components in a

multi-component gas mixture having a temperature of
about 400°C or more, comprising:

(a) providing within the gas mixture an array
of at least three chemo/electro-active
materials, each chemo/electro-active
material having a different electrical
response characteristic upon exposure to
each of the individual analyte gas
components than each of the other
chemo/electro-active materials, wherein at
least one chemo/electro-active material,
when at a temperature of about 400°C or
more, (i) has an electrical resistivity in
the range of about 1 ohm-cm to about $10^5$
ohm-cm, and (ii) exhibits a change in
electrical resistance of at least about
0.1 percent upon exposure of the material
to an analyte gas component, as compared
to the resistance before exposure;

(b) determining an electrical response of each
chemo/electro-active material upon
exposure of the array to the unseparated
components of the gas mixture; and

(c) calculating the concentration of each of
the individual analyte gas components from
the electrical responses of the
chemo/electro-active materials upon
exposure to the multi-component gas
mixture only.

82. A method according to Claim 81 wherein the gas
mixture is an emission from a combustion process.

83. A method according to Claim 81 wherein the
temperature of each chemo/electro-active material is
determined substantially only by the variable
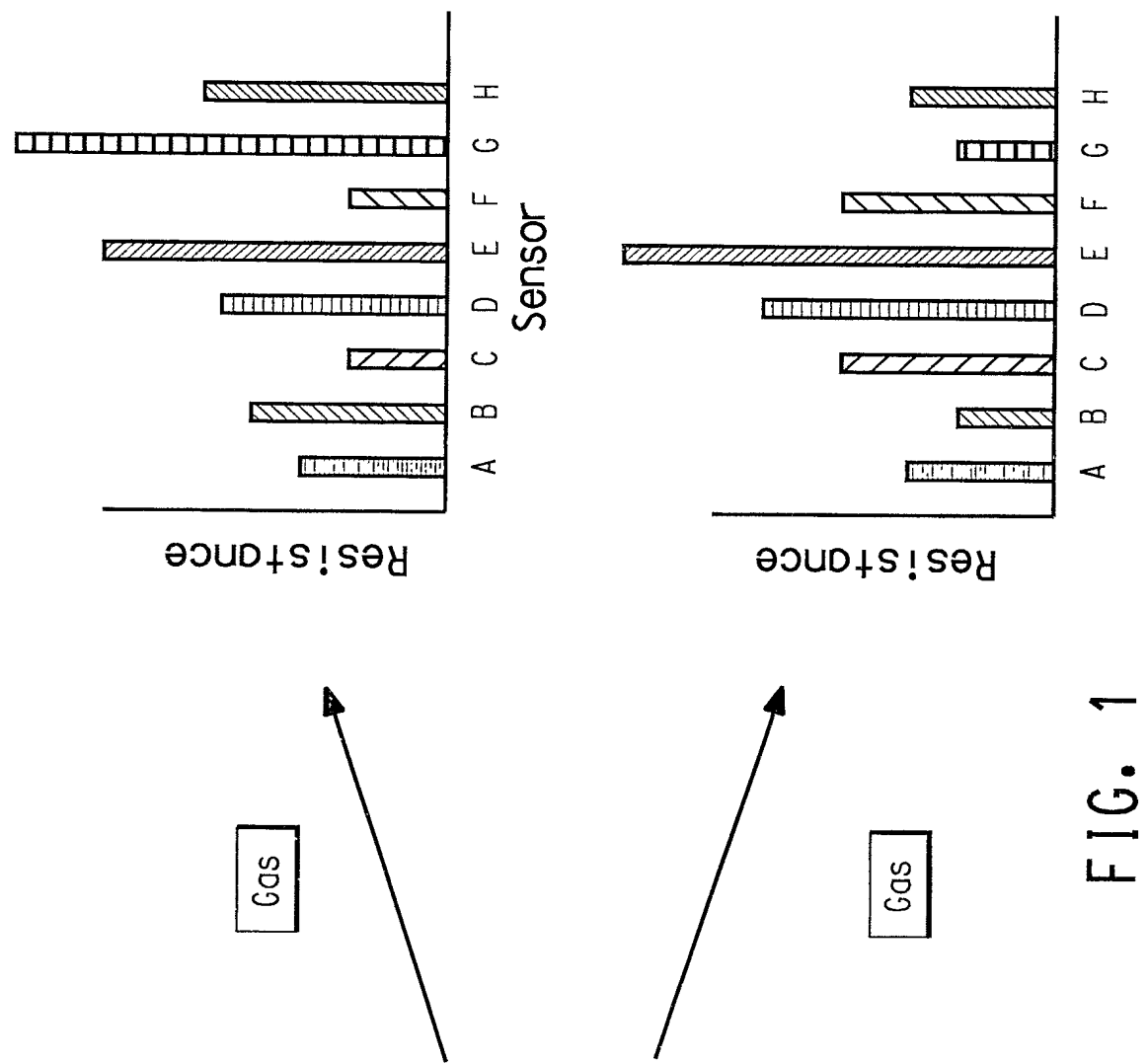temperature of the gas mixture.

84. A method according to Claim 81 wherein the
electrical response characteristic of each material
upon exposure to the gas mixture at a selected

temperature is quantifiable as a value, and the
response value of at least one material is constant or
varies by no more than about twenty percent during
exposure of the material to an analyte gas component at
5      the selected temperature for a period of at least about
one minute.

86. A method according to Claim 81 wherein the
electrical response is selected from the group
consisting of resistance, impedance, capacitance,
10     voltage or current.

86. A method according to Claim 81 wherein at least
one chemo/electro-active material is a metal oxide.

87. A method for analyzing at least one individual
gas component in a multi-component gas mixture,
15     comprising:

(a)    providing an array of at least two
chemo/electro-active materials, each
chemo/electro-active material having a
different electrical response
20                    characteristic upon exposure at a selected
temperature to the individual gas
component than each of the other
chemo/electro-active materials, the
electrical response characteristic of each
25                    material being quantifiable as a value,
wherein the response value of at least one
material is constant or varies by no more
than about twenty percent during exposure
of the material to an individual gas
30                    component at the selected temperature for
a period of at least about one minute;

(b)    determining the electrical response value
of each chemo/electro-active material upon
exposure of the array to the gas mixture;
35                    and

(c)    performing an analysis of the individual
gas component from the electrical response
values.

88. A method according to Claim 87 wherein the array is situated within the gas mixture, which has a temperature of about 400°C or more.

89. A method according to Claim 87 wherein the gas mixture is an emission from a combustion process.

90. A method according to Claim 87 wherein the analysis performed comprises calculating the concentration within the gas mixture of the individual gas component.

91. A method according to Claim 87 wherein the temperature of each chemo/electro-active material is determined substantially only by the variable temperature of the gas mixture.

92. A method according to Claim 87 wherein the electrical response is selected from the group consisting of resistance, impedance, capacitance, voltage or current.

93. A method according to Claim 87 wherein at least one chemo/electro-active material is a metal oxide.

94. A method according to Claim 87 wherein the array is situated in the gas mixture, which has a temperature of less than about 400°C, and the array has a substantially constant temperature of about 400°C or more.

FIG. 1
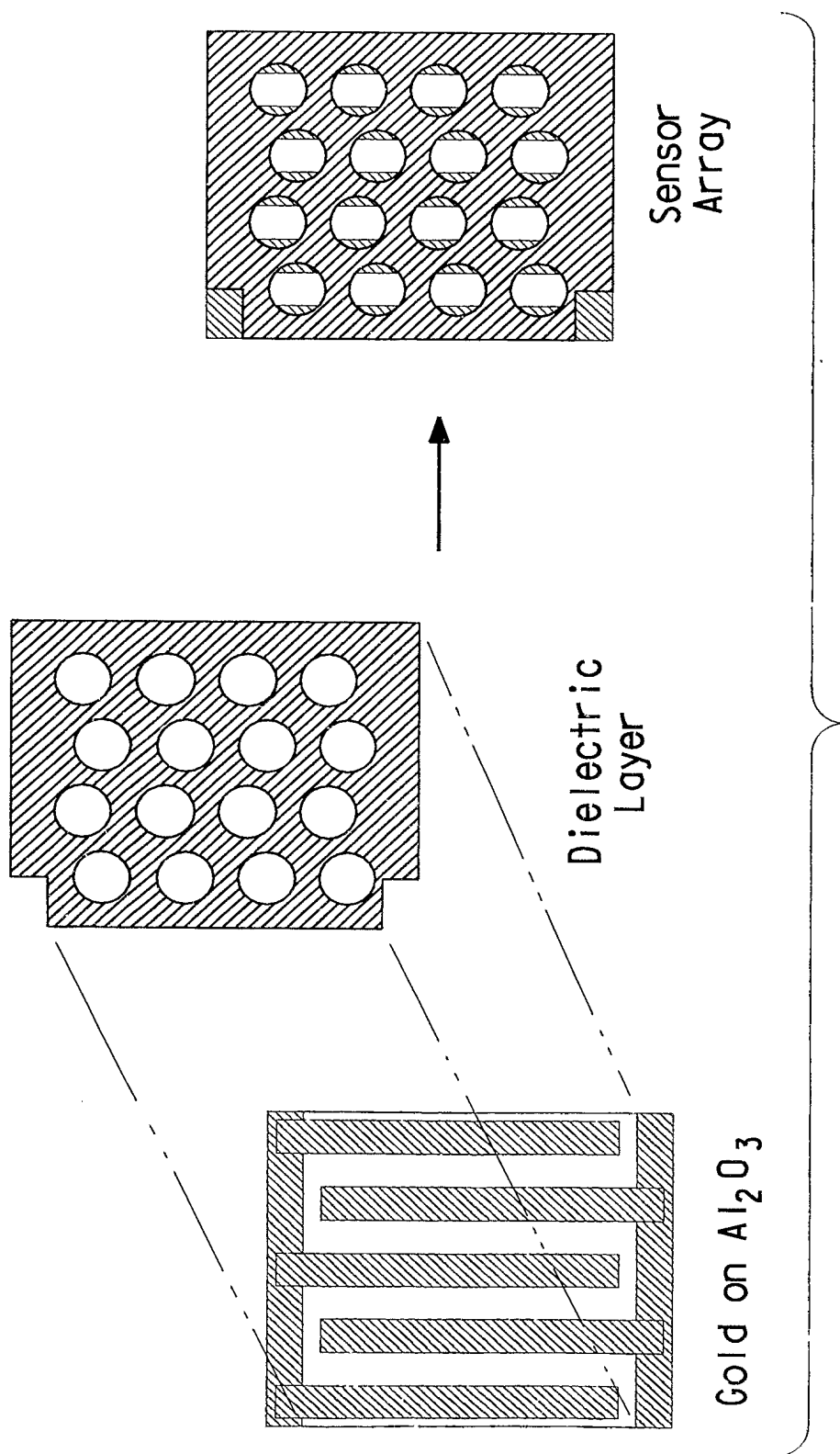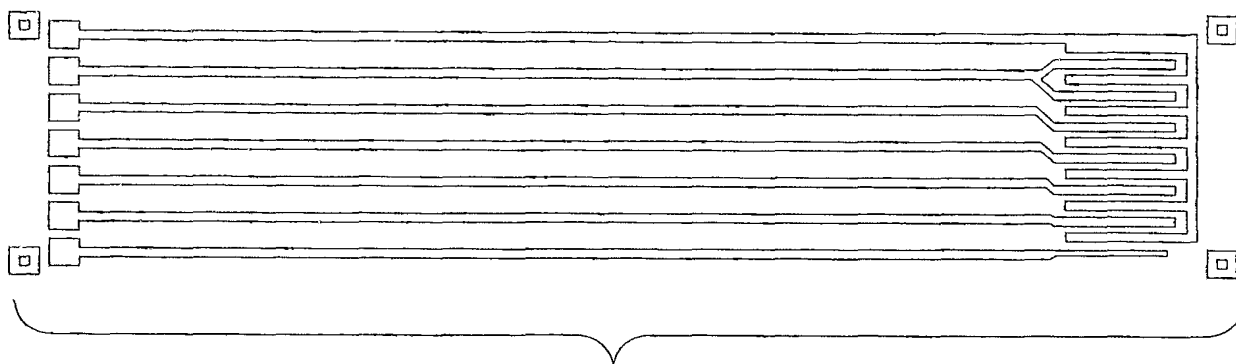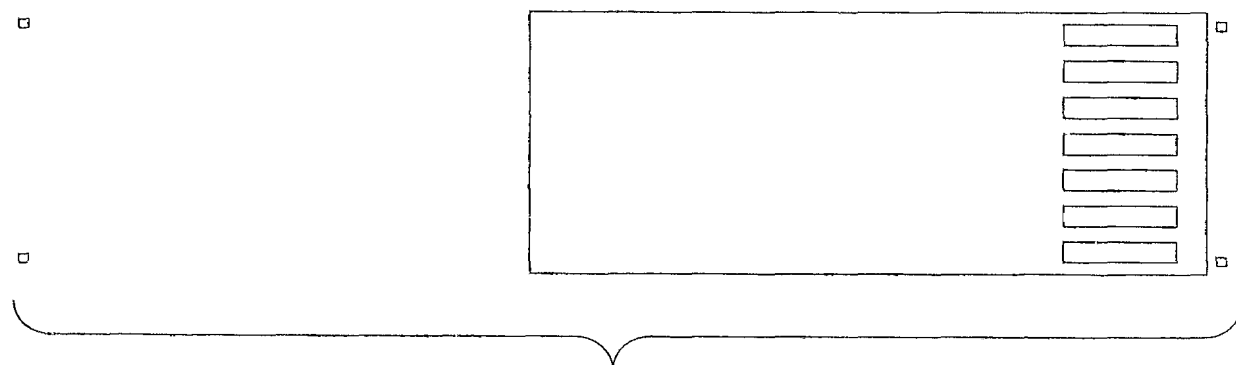
FIG. 2

Sensor Array

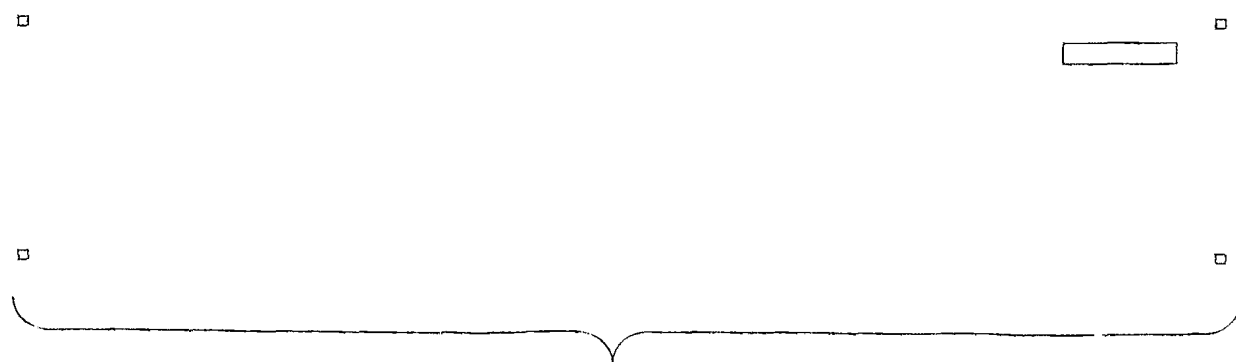Dielectric Layer

Gold on $Al_2O_3$

FIG. 3A



FIG. 3B



FIG. 3C